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Aerosol Chemistry and Air-Snow Transfer in Coastal Antarctica

by

Julie Suzanne Hall

**A Thesis Submitted
For The Degree Of Doctor Of Philosophy
To The Open University**

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Natural Environmental Research Council
Madingley Road
Cambridge, UK**

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Abstract

The aims of this dissertation are to better understand the sources of aerosol particles reaching coastal Antarctica, and the processes that control aerosol deposition to the snow surface and inclusion into the ice.

Daily collections of aerosol particles and surface snow samples were made from British Antarctic Survey base, Halley. Aerosol and snow sea salt were found to have maximum concentrations during the austral winter and non sea salt sulphate and methanesulphonic acid concentrations peaked during the summer, confirming previous work by other authors.

These species were compared with local meteorological events (such as wind speed and direction) to identify a source for particularly high concentration events. Winter sea salt was found to have a local source, consisting probably of concentrated brine pools on surfaces of freshly formed sea ice and needle-like structures, known as frost flowers, which form from the pools. The sea salt component of these high events was also found to be fractionated, with a deficit of sodium sulphate (mirabilite). Methanesulphonic acid and non sea salt sulphate did not appear to have a local source. Instead, using back trajectories of air mass origins to identify a longer range aerosol source, high concentration events were associated with the air mass having passed over an area of open water several days before reaching Halley.

The processes of aerosol deposition to the snow surface were then quantified. Dry, fog and wet deposition, sublimation, wind pumping, blowing and drifting snow were examined experimentally and theoretically. For this coastal Antarctic location, wet deposition was found to be highly dominant (80%). Dry deposition accounted for about 10% and drifting and blowing snow were found to be important in determining whether a snowfall event remained recorded in the accumulated snow record, and ultimately in any ice core.

This thesis has suggested that for sea salt, methanesulphonic acid (MSA) and non sea salt sulphate, there may be an alternate way of interpreting concentrations of these species in coastal Antarctic ice cores. Rather than an indication of increased storminess and long range transport, high loadings of sea salt could actually give information on the extent of new, fresh sea ice and could therefore be used to infer the local temperature, sea ice extent and possible wind direction at the time of core formation. Elevated MSA and non sea salt sulphate concentrations in ice cores could also give us information on the extent of open water and not simply an increase in marine biogenic activity and DMS emissions.

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List of Figures

1.1: General map of Antarctica, showing significant ice core drillings and sites of continuous aerosol measurements.....	15
1.2: Position of the three bases involved in the collaborative sampling programme.....	16
1.3: A sketch map of the Brunt Ice Shelf in the Halley region.....	17
1.4: Mean monthly temperatures at Halley, Jan 1991 - Feb 1993.....	18
1.5: Typical wind rose for Halley.....	19
2.1: The relative positions of Halley 4 and Halley 5.....	59
2.2: The sampling sites at Halley 4 and 5.....	59
2.3: Filter sampling set-up at Halley.....	60
2.4: Simulated two-way valve set-up. (a) Intended filter/two way valve sampling set-up and (b) actual valve set-up.....	60
2.5: Graphical representation of the efficiency of extraction of particles from filters, for the major anionic species.....	61
2.6: Surface snow sampler.....	62
2.7: Accumulated snow sampler.....	62
2.8: Position of samples collected on sastrugi.....	63
2.9: Example chromatogram using ion chromatograph method 3.....	64
2.10: Example chromatogram using ion chromatograph method 4.....	65
2.11: Ion chromatography calibration plots for MSA^- , Cl^- , Br^- , NO_3^- and SO_4^{2-}	66
2.12: Ion chromatography calibration plots for Na^+ , K^+ , Mg^{2+} and Ca^{2+}	67

2.13: Atomic absorption spectrophotometry calibration plots for Na^+ and Mg^{2+}	68
2.14: Flame emission spectrophotometry calibration plot for K^+	68
2.15: Observed deviations from the true concentration in inter-laboratory comparison study.....	69
3.1: Daily, raw data for aerosol sea salt components measured at Halley.....	139
3.2: Monthly averages for aerosol sea salt components measured at Halley.....	140
3.3a: Daily, raw data for aerosol sea salt, measured at Halley.....	141
3.3b: Monthly averages for aerosol sea salt measured at Halley.....	141
3.4: Location of other sea salt measuring Antarctic bases.....	142
3.5: Particle behaviour at sampling inlets under non-isokinetic conditions.....	142
3.6a High episodes of aerosol sea salt at Halley during 1991, plotted with associated wind speed and direction.....	143
3.6b: High episodes of aerosol sea salt at Halley during 1992, plotted with associated wind speed and direction.....	144
3.7a: Close up of frost flowers.....	145
3.7b: An expanse of newly formed ice, covered by frost flowers, located 15 km to the west of Halley.....	145
3.8: Scatter plot for non sea salt sulphate versus sodium for the complete Halley aerosol record.....	146
3.9: Scatter plots of the major cations versus sodium.....	147
3.10: Sulphate to sodium ratios on days of high aerosol sea salt, plotted with the bulk sea water ratio for sulphate to sodium.....	148
3.11: Representative high episodes of aerosol sea salt at Halley during 1991 and 1992, plotted with associated daily surface temperature.....	149
3.12: Possible sources of sulphate present in Antarctica.....	150
3.13: Flow diagram highlighting the key stages in biogenic sulphur production.....	151

3.14: Black carbon data and daily aerosol sulphate concentrations for two periods in 1992.....	152
3.15: Corrected nss sulphate and nss sulphate calculated using 0.252 as BSW ratio.....	153
3.16: Daily, raw data for aerosol corrected non sea salt sulphate and methane sulphonic acid at Halley.....	154
3.17: Monthly averages for aerosol nss sulphate and MSA at Halley.....	155
3.18a: Atmospheric DMS seasonal cycle from Cape Grim, Tasmania.....	156
3.18b: Atmospheric DMS seasonal cycle from Neumayer station, Antarctica.....	156
3.19: Aerosol non sea salt sulphate seasonal cycles at four Antarctic stations, plotted as 10 day averages and monthly mean chlorophyll concentrations from latitudes higher than 50°S, higher than 60°S and between 50 and 60°S.....	157
3.20: Aerosol non sea salt sulphate and MSA concentrations, plotted with corresponding local temperature.....	158
3.21: Seasonal time series of aerosol MSA/nss sulphate at Halley. Both corrected and traditional nss sulphate concentrations have been used.....	159
3.22: Scatter plot of nss sulphate versus MSA aerosol concentrations at Halley.....	160
3.23: High episodes of aerosol methane sulphonic acid at Halley, plotted with associated wind speed and direction.....	161
3.24: Average MSA and non sea salt sulphate concentrations during particular wind directions. Wind direction is plotted against frequency of days.....	162
3.25: Average summer MSA and summer non sea salt sulphate concentrations during particular summer wind directions. Wind direction is plotted against frequency of days.....	162
3.26a: MSA and nss sulphate concentrations in snow and ice, with distance inland from the coast.....	163
3.26b: Sea salt concentrations in snow and ice, with distance inland from the coast.....	163
3.27: Representative back trajectory classifications: continental coastal (Cc), continental interior (Co), marine coastal (Mc) and marine open water (Mo).....	164

3.28: Back trajectories for the 25 February 1992, a day of high MSA concentration and the 24 February 1992, a day of low MSA concentration.....	165
3.29: Weekly composite sea ice coverage chart for the week ending 24 February 1992.....	166
3.30: Back trajectories for the 11 March 1992, a day of high MSA concentration and the 10 March 1992, a day of low MSA concentration.....	167
3.31: Weekly composite sea ice coverage chart for the week ending 12 March 1992.....	168
3.32: Back trajectory for the 19 May 1992, a day of high sea salt concentration.....	169
3.33: Weekly composite sea ice coverage chart for the week ending 21 May 1992.....	170
4.1: Daily, raw sea salt concentrations in surface snow and monthly averages.....	187
4.2: Monthly averages for snow sea salt components measured at Halley.....	188
4.3a: Individual events of the highest aerosol sea salt variability and the corresponding snow concentrations for those days in 1991.....	189
4.3b: Individual events of the highest aerosol sea salt variability and the corresponding snow concentrations for those days in 1992.....	190
4.4: Closer examination of daily aerosol and snow sea salt concentrations at Halley, looking at specific months in the time series.....	191
4.5: Individual events of the highest snow sea salt variability and the corresponding aerosol concentrations for those days.....	192
4.6: Scatter plot for non sea salt sulphate versus sodium for the complete Halley aerosol record.....	193
4.7: Daily raw non sea salt sulphate concentrations in surface snow at Halley and monthly averages.....	194
4.8: Corrected daily nss sulphate and traditionally calculated nss sulphate.....	195
4.9: Daily raw MSA concentrations in surface snow at Halley and monthly.....	196

4.10: Episodes of high MSA loadings in daily the aerosol and snow record at Halley, looking at specific days in the time series.....	197
4.11: Closer examinations of daily aerosol and snow MSA concentrations at Halley, looking at specific months in the time series.....	198
4.12: Individual events of the highest snow MSA variability and the corresponding aerosol concentrations for those days.....	199
4.13: Halley snow samples, s1 and s2, plotted against one another for sea salt, MSA and corrected nss sulphate.....	200
4.14: Sea salt concentration in surface snow, after three events of drift, at each of the nine stakes.....	201
5.1: Integrated accumulation of snow at Halley, measured at a single stake, close to the sampling area for daily surface snow collection.....	243
5.2: Concentrations of sea salt in surface snow at Halley when there was no significant accumulation measured at a snow stake.....	244
5.3: Concentrations of MSA in surface snow at Halley when there was no significant accumulation measured at a snow stake.....	245
5.4: Sea salt concentrations for three events when no snowfall, drifting or blowing snow, or fog occurred and no accumulation was measured at the snow stake.....	246
5.5: Scatter plot of daily changes in surface snow concentration against aerosol concentration at Halley for sea salt, on days when there was no significant accumulation and the daily concentration changes was limited to less than 100 ng g ⁻¹	247
5.6: Deposition velocity versus particle diameter over snow at Dye 3, Greenland, based at a 10 cm height.....	247
5.7: Schematic diagram of the sea salt concentrations in ng m ⁻³ , found in six sastrugi features at Halley, during summer 1995.....	248
5.8: Scatter plot of accumulated snow concentration (fresh snowfall) against the preceding 24 hour aerosol concentration.....	249
5.9: Concentrations of rime at three levels above the snow surface and also the concentration of surface snow at the site.....	250

6.1: Two years of accumulated snow for chloride, sampled at Halley 4 and 5, and firn core 1, collected from Halley 5, after 2 years of snow sampling.....257

6.2: One year of accumulated snow for chloride and firn core 2 (Halley 4) and firn core 3 (Halley 5), sampled after 1 year of snow collection, at Halley 4.....258

6.3: Two years of accumulated snow for MSA, sampled at Halley 4 and 5, and firn core 1, collected from Halley 5, after 2 years of snow sampling.....259

6.4: Smoothed signal of two years of accumulated snow for MSA, sampled at Halley 4 and 5, and firn core , collected from Halley 5, after 2 years of snow sampling.....260

6.5: One year of accumulated snow for MSA and firn core 2 (Halley 4) and firn core 3 (Halley 5), sampled after 1 year of snow collection, at Halley 4.....261

List of Tables

1.1: The occurrence of precipitation over the 2 year time period of this project, at Halley.....11

2.1: Dates of when and how filters were treated.....24

2.2: Manufacturers details of filters used.....26

2.3: Aerosol field blank values.....35

2.4: Analytical blank values.....37

2.5: Filter detection limits.....37

2.6: Depths from which accumulated snow samples were taken.....41

2.7: Snow Sample Detection Limits.....42

2.8: Acknowledgement of who prepared and collected the samples available.....47

2.9: Analysts involved in this project.....47

2.10: Summary of the methods used in ion chromatography.....49

2.11: Summary of the methods used to analyse the various samples.....53

2.12: Ratios of the ions in each of the standard solutions.....54

2.13: Results of interlaboratory sample A analysis.....56

2.14: Results of interlaboratory sample B analysis.....56

2.15: Calibration ranges for the analytes in the interlaboratory experiment.....57

2.16: Summary results of interlaboratory tests.....57

3.1: The concentration of the major ions in sea water.....72

3.2: Mean monthly concentrations for MSA, corrected nss sulphate and traditional nss sulphate.....109

3.3: Summary of MSA and non sea salt sulphate aerosol concentrations.....110

3.4: Distance of Halley and Neumayer from the ice edge during the Austral summer.....111

3.5: Average aerosol MSA/nss SO₄²⁻ monthly ratios for Halley.....115

3.6: Back trajectory predictions for the location of air parcels 1 to 5 days prior to arrival at Halley, run over days when particularly high MSA aerosol concentrations were observed.....135

3.7: Back trajectory predictions for the location of air parcels 1 to 5 days prior to arrival at Halley, run over days when particularly high sea salt aerosol concentrations were observed.....136

4.1: Sea salt concentration in samples s1 and s2.....184

5.1: The occurrence of precipitation over the 2 year time period of this project, at Halley.....219

5.2: Estimates of the annual dry deposition flux at Halley, during 1991 and 1992.....224

5.3: Measurements of sastrugi at Halley, during summer 1995.....228

5.4: Estimates of the annual wind pumping deposition flux at Halley, during 1991 and 1992.....230

5.5: Other reported scavenging ratios (W) for Antarctica, Greenland and North America.....236

5.6: Estimates of the annual wet deposition flux at Halley during 1991 and 1992.....240

5.7: Estimates of the annual deposition flux at Halley due to scavenging by blown or drifted snow, during 1991 and 1992.....243

5.8: Estimates of the annual deposition flux at Halley due fog depositing rime, during 1991 and 1992.....250

5.9: Summary of the annual deposition flux contributions to Halley.....251

5.10: Percentage contribution the various deposition processes make to the annual flux at Halley.....252

Contents

Abstract.....	i
Acknowledgement.....	iii
List of Figures.....	v
List of Tables.....	xi
Contents.....	xiii

Chapter 1: Introduction

1.1	Antarctica.....	01
1.2	The Importance of Ice Cores.....	02
1.3	Aerosol and Ice Core Collections in Antarctica.....	04
	1.3.a The Antarctic Peninsula.....	05
	1.3.b Central Antarctica.....	05
	1.3.c Coastal Antarctica.....	06
1.4	A Collaborative Sampling Programme.....	07
1.5	Halley Station.....	07
	1.5.a Physical Factors.....	07
	1.5.b Climatic Factors.....	09
	1.5.b(i) Temperature Observations at Halley.....	09
	1.5.b(ii) Precipitation.....	10
	1.5.b(iii) Wind.....	11
	1.5.b(iv) Sea Ice.....	12
1.6	Aims of this Study.....	13
	Figures.....	15

Chapter 2: Sample Collection and Analytical Techniques

2.1	Introduction.....	21
2.2	Aerosol Sampling at the British Antarctic Survey.....	21
2.3	Rationale for the Sampling Protocol at Halley, for this Thesis.....	22
	2.3.a Samples Collected.....	23
2.4	The Aerosol Record	24
	2.4.a Cleaning Procedures.....	24
	2.4.a(i) Daily Aerosol Record.....	24
	2.4.a(ii) Weekly Aerosol Record.....	25
	2.4.b Sampling Procedure.....	26
2.5	Volume of Air Pumped.....	28
	2.5.a Two-Way Valve Set-Up.....	29
	2.5a.(i) Results and Discussion of Hypothesis.....	29

2.6	Extraction of the Aerosol Phase.....	30
2.6.a	Extraction Efficiency.....	32
2.7	Filter Blanks.....	33
2.7.a	Test Filters.....	34
2.7.b	Field Blanks.....	34
2.7.c	Analytical Blanks.....	36
2.7.d	Filter Detection Limits.....	37
2.8	Local Contamination of Filters.....	38
2.9	The Snow Record	38
2.9.a	Cleaning Procedures.....	39
2.9.b	Sampling Procedure.....	39
2.9.b(i)	Surface Snow.....	40
2.9.b(ii)	Accumulated Snow.....	40
2.10	Detection Limits and Snow Blanks.....	41
2.11	Other Snow Samples.....	42
2.11.a	Drifting Snow.....	42
2.11.b	Sastrugi - Wind Pumping.....	43
2.11.c	Rime Samples.....	44
2.12	The Firn Core Record	45
2.12.a	Drilling of the Firn Cores.....	45
2.12.b	Sub-sampling of the Firn Cores.....	46
2.13	Acknowledgement.....	46
2.14	Sample Analysis	47
2.14.a	Ion Chromatography.....	47
2.14.a(i)	Method 1: Anions.....	49
2.14.a(ii)	Method 2: Cations.....	50
2.14.a(iii)	Method 3: Anions.....	50
2.14.a(iv)	Method 4: Cations.....	51
2.14.b	Atomic Absorption Spectrophotometry.....	51
2.14.c	Flame Emission Spectrophotometry.....	52
2.15	Standards.....	53
2.16	Interlaboratory Analytical Tests.....	54
2.16.a	Interlaboratory Test Results.....	55
2.17	Conclusions.....	58
	Figures.....	59

Chapter 3: Aerosol Chemistry in Coastal Antarctica

3.1	Introduction.....	71
3.2	Sea Salt Species	72
3.2.a	Sea Salt Aerosol Sources.....	72
3.2.b	Sea Salt Size Distribution.....	73
3.2.c	The Significance of Sea Salt.....	74
3.2.d	Determination of Aerosol Sea Salt Concentrations.....	76
3.3	Seasonality of Aerosol Sea Salt at Halley.....	76
3.3.a	Other Reported Aerosol Sea Salt Records.....	82

3.4	Daily Variability in Aerosol Sea Salt.....	82
3.4.a	Additional Source of Winter Aerosol Sea Salt.....	84
3.5	Fractionation of Sea Salt.....	87
3.5.a	High Events of Airborne Sea Salt.....	90
3.6	Aerosol Sea Salt and Temperature.....	92
3.7	Conclusions and Recommendations.....	92
3.8	Sulphur Species	96
3.8.a	Particle Formation and Size Distribution.....	96
3.8.b	Sulphur Aerosol Sources.....	97
3.8.b(i)	Marine Biogenic Sulphur.....	97
3.8.b(ii)	Volcanic Sulphur.....	100
3.8.b(iii)	Continental Sulphur.....	101
3.8.b(iv)	Anthropogenic Sulphur.....	102
3.8.c	Significance of Biogenic Sulphur Species.....	103
3.8.d	Determination of Non Sea Salt (or excess) Sulphur.....	104
3.9	Seasonality of Non Sea Salt Sulphate and MSA.....	106
3.9.a	Monthly Variability.....	106
3.9.b	Annual Mean Concentrations: in comparison with other reported Antarctic aerosol records.....	110
3.9.c	MSA to Non Sea Salt Sulphate Aerosol Weight Ratio (R).....	113
3.9.c(i)	Non Biogenic Non Sea Salt Sulphate.....	115
3.10	Daily Variability in MSA.....	116
3.10.a	Local Conditions.....	117
3.11	Regional Conditions: Back Trajectory Analysis	120
3.11.a	Introduction.....	120
3.11.b	The Trajectory Model.....	122
3.11.c	Trajectory Classification.....	124
3.11.d	Consistency of Trajectory Model.....	125
3.11.e	Trajectory Results.....	126
3.11.f	Methanesulphonic Acid Aerosol.....	126
3.11.f(i)	Conclusions: MSA.....	130
3.11.g	Sea Salt Aerosol.....	130
3.11.g(i)	Conclusion: Sea Salt.....	132
3.11.h	Overall Back Trajectory Conclusion.....	132
	Figures.....	132

Chapter 4: Snow Chemistry in Coastal Antarctica

4.1	Introduction.....	171
4.2	Snow Sea Salt	171
4.2.a	Seasonality.....	172
4.2.b	Variability in Snow Sea Salt.....	174
4.3	High Aerosol Concentrations: are they seen in the snow record?.....	175
4.4	High Snow Concentrations: are they seen in the aerosol record?.....	176
4.5	Fractionation of Snow Sea Salt.....	177
4.6	Snow Sulphur Species	178

4.6.a	Seasonality.....	179
4.6.b	Variability in Sulphur Species.....	180
4.7	High Aerosol Concentrations: are they seen in the snow record?.....	181
4.8	High Snow Concentrations: are they seen in the aerosol record?.....	181
4.9	General Relationship Between Aerosol and Snow Chemistry	182
4.10	Spatial Variability.....	182
4.10.a	Drifting Snow Experiment.....	184
	Figures.....	187

Chapter 5: Aerosol Deposition Processes in Antarctica

5.1	Introduction.....	203
5.2	The Air-Snow Transfer Function.....	204
5.3	Dry Deposition Process.....	204
5.3.a	Calculation of the Dry Deposition Flux.....	206
5.4	Experimental Estimates of Dry Deposition.....	207
5.4.a	Method One.....	207
5.4.b	Method Two.....	209
5.4.c	Method Three.....	210
5.4.d	Conclusion.....	211
5.5	Model Estimates of Dry Deposition.....	212
5.5.a	The Annual Dry Deposition Flux.....	214
5.6	Wind Pumping Process.....	215
5.6.a	Experimental Estimates of Wind Pumping.....	217
5.6.b	Theoretical Estimates of Wind Pumping.....	219
5.7	Sublimation Process.....	220
5.8	Wet Deposition Process.....	221
5.8.a	Calculation of the Wet Deposition Flux.....	223
5.8.b	Scavenging Ratios.....	223
5.8.b(i)	Method One.....	224
5.8.b(ii)	Method Two.....	225
5.8.b(iii)	The Significance of Scavenging Ratios.....	225
5.8.c	Accumulated Snow.....	228
5.9	Drifting and Blowing Snow Processes.....	230
5.10	Fog Deposition.....	234
5.10.a	Calculation of the Fog Deposition Flux.....	235
5.10.b	Experimental Estimate of Fog Deposition.....	236
5.10.b(i)	Rimed Snow Experiment.....	237
5.10.c	Model Estimate of Fog Deposition.....	238
5.11	The Importance and Contribution of the Various Deposition Processes.....	241
	Figures.....	243

Chapter 6: Shallow Firn Cores in Coastal Antarctica

6.1	Introduction.....	251
6.2	Sea Salt Species in Shallow Firn Cores	252

6.2.a	Core 1.....	252
6.2.b	Cores 2 & 3.....	254
6.3	MSA in Shallow Firn Cores.....	254
6.3.a	Core 1.....	254
6.3.b	Cores 2 & 3.....	256
6.4	Conclusions.....	256
	Figures.....	257

Chapter 7: Conclusions

7.1	Introduction.....	263
7.2	Summary.....	263
7.2.a	The Source of Winter Sea Salt Aerosol at Halley.....	263
7.2.b	The Source of MSA and Non Sea Salt Sulphate Aerosol at Halley.....	265
7.2.c	Snow Record - Sea Salt and MSA.....	267
	7.2.c(i) High Aerosol Concentrations: are they seen in the snow record?.....	267
	7.2.c(ii) High Snow Concentrations: are they seen in the aerosol record?.....	268
7.2.d	Aerosol Deposition Processes.....	268
7.2.e	Preservation of Coastal Antarctic Snow into Shallow Firn.....	269
7.3	Implications for Ice Core Interpretation.....	269
7.4	Future Work.....	270
7.5	Have the Aims of this Thesis Been Met?.....	274
	References.....	275

Chapter 1

Introduction

1.1 Antarctica

Antarctica - a land of extremes, a cold quiet wilderness, surrounded by a stormy sea, and yet as early as the 18 th century, explorers and scientists alike recognised the Antarctic's potential, striving to conquer it. Many were unsuccessful and it still remains the worlds last truly pristine environment. Even the surface of the moon is better mapped than some parts of Antarctica.

It is the coldest place on Earth, with record low temperatures down to -89°C . The fifth largest continent, it is the windiest and also the highest place on Earth, with an average height three times greater than that of other continents. Surrounded by the Southern Ocean, by the end of the summer, in early February, approximately 3 million km^2 of local sea is covered by ice. With the onset of winter and the months of perpetual darkness, this increases to as much as 20 million km^2 . This seasonal difference between the maximum and minimum sea ice cover is greater than the total area of Antarctica itself, approximately 14 million km^2 [Walton, 1987].

The Antarctic Peninsula (see figure 1.1) receives more snowfall than the rest of the continent, contrasting with the central plateau, technically classed as a desert. Exposed rock surfaces account for less than 2% of Antarctica's surface, the rest of the continent being covered by snow and ice. The ice sheet itself comprises 90% of the world's fresh water, and if it were to melt the mean sea level would rise by 65 m.

Over the years, man has had little impact on Antarctica. The continent remains remote from all centres of population, with no indigenous people. The few transitory inhabitants consist mainly of scientists and support staff, maintaining the remote research bases. Tourism is beginning to play a role in some sub-Antarctic regions, but the harshness of the terrain will inevitably limit this. As a result of the lack of man-made activity, Antarctica can be viewed as the cleanest natural laboratory in the world. It is the ideal place to study changes in the Earth's natural chemical cycles, where the local atmosphere and snow are largely unaffected by anthropogenic sources. The potential does, however, exist for some anthropogenic impurities, from long range sources, to be measured in the snow and ice core records.

1.2 The Importance of Ice Cores

Ice forms as successive layers of snow are compacted down, year after year, gradually forming firn and then ice. In polar ice sheets, where there is little or no melting, drilled ice cores can act as a library for past precipitation and have been used as a cornerstone for predicting the Earth's future climate. Included in them are samples of the atmosphere, such

as non-reactive trace gases in air bubbles (methane and carbon dioxide), oxygen isotopes (used to age an ice core) and trapped aerosols (chemical particles). It is this latter component that is of interest to this study.

Until quite recently, it has been assumed that concentrations of chemical species found in ice cores could be **directly** (or a linear relationship), extrapolated back to the concentration of that species in the atmosphere, when it originally became deposited on the snow surface. For some species, such as non-reactive trace gases like methane [Raynaud et al., 1993], this back extrapolation to a past atmosphere is possible and is well calibrated.

However, for reactive gases and particulate material, the attractive assumption that a 'linear' relationship exists between changes in ice concentrations and changes in a past atmosphere and snow concentrations, is not necessarily true. In the past, authors have suggested that ice core sea salt data can directly be used to derive sea ice extent [Peel & Mulvaney, 1992], and are associated with increased storminess [Petit et al., 1981]. The extent of marine biological productivity has also been directly linked to methanesulphonic acid (MSA) concentrations [Legrand & Feniet-Saigne, 1991], past volcanism to sulphate and acidity measurements, and atmospheric circulation patterns to dust levels [Cragin et al., 1977; Mayewski et al., 1994].

In recent years, increased caution has been used in extrapolating from ice core data to a past atmospheric concentration. It is now recognised that not only the original atmospheric make-up above the ice core drill site, but how the aerosol record is then incorporated into

the surface snow, must also be taken into account when interpreting the final ice core record. Many different processes control how aerosols are deposited into the snow, such as dry, wet and fog deposition, wind pumping, sublimation, drifting and blowing snow. Once deposited, the concentration can be altered by various post depositional processes. If these mechanisms, by which the chemical species are incorporated into the snow record, are not themselves fully understood, then the ice core record alone is of little use to us.

1.3 Aerosol and Ice Core Collections in Antarctica

To date, relatively little has been invested in improving our understanding of the relationship that exists between the air, snow, firn and ultimately the ice cores. This is despite the fact that over the last 20 years an increasing number of cores have been drilled throughout the Arctic and Antarctic. One of the reasons for this is that labour intensive, year round programmes are needed to collect daily aerosol samples, which could account for daily oscillations, translated into seasonal cycles, in the ice core record. Only a minority of Antarctic stations have undertaken such programmes and most of these have not then been compared to snow and ice compositions.

Taking Antarctica in three separate segments, the Peninsula, central and coastal Antarctica, and without trying to give a comprehensive list of all ice drilling sites, it is evident that many ice core projects have taken place. Figure 1.1 is a general map of Antarctica showing significant ice core drillings, sites of continuous aerosol measurements and scientific research bases mentioned throughout this thesis.

1.3.a The Antarctic Peninsula

A number of significant ice cores have been drilled on the Antarctic Peninsula to date. These include cores drilled at Siple Station, situated at the base of the Peninsula [Mosley-Thompson et al., 1991], at a site known as Gomez Nunatak [Mulvaney et al., 1992], [Mulvaney & Wolff, 1993], on the Dyer Plateau [Mulvaney et al., 1992], on the Beethoven Peninsula [Mulvaney & Wolff, 1994] and on Dolleman Island [Peel et al., 1988; Mulvaney et al., 1992; Mulvaney & Wolff, 1993]. Considering the number of cores collected, the aerosol data set available for this area, is surprisingly small. For the Peninsula, continuous aerosol measurements were made at two stations, Palmer (64.77°S, 64.05°W) and Marsh (62.18°S, 58.30°W). Weekly filter samples were collected for 3 and 13 months respectively at these bases and analysed for sodium, sulphate, nitrate, methanesulphonic acid, ammonium, ²¹⁰Pb and ⁷Be [Savoie, et al., 1993]. Two months of aerosol sampling (January and February 1994) were also undertaken at Palmer station, for methanesulphonic acid and non sea salt sulphate [Berresheim, 1998]. During this study, DMS (dimethylsulphide) concentrations were also monitored in air and sea water.

1.3.b Central Antarctica

Central Antarctica also lacks an adequate, continuous aerosol data set. Limited information is available from South Pole Station, however this analysis does not cover as many species as those typically studied in ice cores [Shaw, 1988; Bodhaine, 1996]. Once more there are many more ice core records, than aerosol data sets. Cores have been drilled from the

Amundsen-Scott base, at South Pole [Legrand & Delmas, 1984], from Byrd Station, in West Antarctica [Herron, 1982] and at sites known as Dome C [Legrand & Delmas, 1988] and Vostok [Legrand et al., 1988], the deepest ice core drilling to date in Antarctica. It is particularly important that we understand the atmospheric/snow exchange processes in this area of Antarctica, as at least four major drilling projects are planned in the forth-coming years [Wolff et al., in press].

1.3.c Coastal Antarctica

The situation for coastal Antarctic is more encouraging, where a greater number of continuous aerosol measurements are available. This is probably due to the larger number of research stations located in the area. However, once again, a full understanding of air-snow processes has not been obtained from coastal Antarctica. Aerosol measurements have been made from Mawson station, [Prospero et al., 1991; Savoie et al., 1992; Savoie et al., 1993] and extensively from Neumayer station [Wagenbach et al., 1988].

Ice cores have also been drilled around the coast in areas such as Dronning Maud Land [Gjessing, 1989] and Coats Land, [Mulvaney & Wolff, 1993; Mulvaney & Wolff, 1994]. A recent major drilling project also took place on Berkner Island, [Mulvaney, personal communication]. Moving to the Eastern Antarctic coast line, Law Dome, 120 km east of Casey station (an Australian station) has also been the site of an ice coring project [Morgan et al., 1997]. Several shallow cores have also been collected along a 430 km coastal-interior traverse, known as the French D-sites [Legrand & Delmas, 1985].

1.4 A Collaborative Sampling Programme

The obvious requirement for year round snow and aerosol measurements brings us back to this project. As a result of the lack of data, a collaborative sampling programme was initiated between the British Antarctic base, Halley, the French base, Dumont D'Urville and the German base, Neumayer. The locations of these scientific bases are shown in figure 1.2. The project was set up to study aerosol and snow chemistry at three Antarctic coastal stations. Each station undertook continuous aerosol measurements and snow sampling, for a period of no less than two years.

This thesis will mainly concentrate on results from Halley base, but with useful comparisons drawn from the other two coastal sites.

1.5 Halley Base

The subsequent chapters in this thesis will use and interpret data collected from Halley Research Station. This section describes the physical and climatic conditions that the base operates under.

1.5.a Physical Factors

The present Halley base is the fifth research station to be built on the Brunt Ice Shelf, Coats Land. The first was established in 1956 by the Royal Society for the International

Geophysical Year, 1957-58. The station was named after the astronomer Edmond Halley, and was commissioned to study aspects of meteorology, glaciology, seismology, radio astronomy, ionospheric physics, aurora and air glow and geomagnetism. The base moves approximately 760 m per year westward, with the ice shelf, towards the Weddell Sea. This area of Antarctica also receives about a metre of snow accumulation per year. Both of these factors require the base to be regularly replaced and resited before being carried away, or crushed by the weight of overlying snow. The first Halley was moved in 1967, and subsequent stations in 1973, 1983 and 1992. The present base Halley 5, in December 1997 was located at $75^{\circ}35'S$, $26^{\circ}27'W$. Figure 1.3 shows a sketch map of the Brunt Ice Shelf in the Halley region.

The Brunt Ice Shelf is about 32 m above sea level at the station and apart from some small sastrugi, sand dune like features created by the effect of winds blowing over the snow surface, is essentially flat. The ice front is 15 km north of Halley and is characterised by 30 m high ice cliffs. During the winter months the Weddell Sea becomes covered with fast ice, (semi-permanent sea ice). This recedes during summer and a several 10's kms wide lead (ice free region between floes, consisting of open water, or very thin ice) extends along the ice front.

The ice shelf is grounded about 40 km south east of the base, at the Hinge Zone. From the ice front, the shelf rises gently to this disturbed area where it meets the Caird Coast. The land then rises steeply towards the continental plateau, reaching a maximum elevation of 1700 m, some 160 km from the station. The surrounding area is completely snow and ice

covered, with no exposed rock surfaces within 200 km [König-Langlo et. al, in press].

Wildlife is fairly sparse at Halley, however a large colony of Emperor Penguins breed on the fast sea ice attached to the coast. Approximately 50 000 adult birds can be found north west of the base, from June to late December, before dispersing along the coast. A second, smaller colony is also located south west of Halley, along the coast.

1.5.b Climatic Factors

Throughout the sampling period of this thesis, various meteorological observations were made at Halley. Synoptic surface observations were performed every 3 hours at the base. These included averaging of 10 m air temperatures, and air pressure reduced to sea level and wind vectors taken at 10 m. Visual cloud and weather observations were also made according to guidelines set up by the World Meteorological Office [WMO, 1983]. Upper air soundings were taken using balloon radiosondes, launched every day to measure vertical profiles of air pressure, temperature, humidity and wind vector. Both sets of data were transmitted into the Global Telecommunication System (GTS) of the WMO and then distributed to the various national weather services. This is also an ongoing project at Halley base.

1.5.b(i) Temperature Observations at Halley

The mean monthly surface temperatures at Halley stay below freezing, although positive

temperatures are possible throughout December to February. The day to day temperature variations tend to be largest in winter. This is due to the pronounced temperature difference between the air masses from the interior and the ocean. The mean annual temperature at Halley is -19.3°C [König-Langlo et al., in press]. Figure 1.4 shows the mean monthly temperatures at Halley for January 1991-February 1993, the time period covered by work in this thesis. The mean annual temperature for the years in question at Halley, is -18.3°C .

1.5.b(ii) Precipitation

The circumpolar trough of low pressure, is the main mechanism for moisture supply to Antarctica. The trough rings the Antarctic between 60° - 70° S and results in many depressions, north of the continents edge. These lows are responsible for much of the precipitation that falls in the coastal region of Halley, and are deepest and closest to the continent during Spring and Autumn. Due to Halley's proximity to the circumpolar trough, the mean air pressure tends to be fairly low, 988.7 hPa [König-Langlo et al., in press].

Measuring the actual amount of precipitation a site receives in Antarctica is difficult, due to the inability to clearly distinguish between blowing, drifting and falling snow.

Precipitation occurs many times throughout the year at Halley. One or more event (an event implies a precipitation code was recorded in a 3-hourly meteorological reading), occurred on 615 days out of the 2 years of sampling (Table 1.1).

Table 1.1: The occurrence of precipitation over the 2 year time period of this project, at Halley.

Precipitation type	No. of events	No. of days
Drifting snow	724	131
Blowing snow	359	44
Snowfall	1161	378
Fog	405	183

1.5.b(iii) Wind

Some coastal areas of Antarctica, such as Halley, experience persistent winds that rush downward off the ice sheet and onto the sea. Known as katabatic winds, this gravity driven phenomenon is an integral component of Antarctica’s natural system. The katabatic wind regime transports cold, dense air masses down from the high interior outwards and downwards towards the coast. Air masses moving from the interior are also affected by the Coriolis force, (an acceleration which air possesses due to the Earth’s rotation) [McIntosh, 1963]. This causes air to veer to the west as it descends, resulting in the prevailing easterly wind direction at Halley. The westerlies at Halley are associated with penetration of synoptic systems.

At Halley, the strongest winds come from 80-90⁰ (easterlies), due to synoptic disturbances and local topography. The secondary direction is from 260⁰ (westerlies). The annual mean wind speed is 6.2 ms⁻¹. Winds from the north are observed in less than 0.5 % of cases. Figure 1.5 shows a typical wind rose for Halley [King, 1989].

1.5.b(iv) Sea Ice

Antarctic sea ice, at its greatest extent, covers approximately 20 million km², an area larger than the continent itself [Gloersen, 1992], and can therefore influence climatic conditions considerably. It caps the upper layer of the ocean, preventing heat or moisture exchange between the ocean and the atmosphere. This has implications for cloud formation, atmospheric stability and the formation of precipitation.

Sea ice also alters the surface albedo, thus affecting the amount of solar radiation absorbed at ground level. An unfrozen ocean would typically have an albedo of 10-15%, whereas sea ice values can be as high as 90%, when covered with fresh snow [King & Turner, in press]. This value will decrease if the ice cover is thin, with lots of leads. A wide lead (of the order 10-20 km) extends along the ice front, during the summer months, near to Halley, in the Weddell Sea. This is created by a westward flowing current, driven by the prevailing easterly winds, around the 65°S region. These leads can affect the climate at coastal stations, where the open water increases the temperature and humidity, especially during winter, giving rise to fogs and riming events.

Coastal polynyas can also form in the sea ice throughout the year. These are areas of open water, in otherwise closed pack ice. They form as a result of persistent katabatic winds, which mechanically force the sea ice away from the coast, opening up areas of water. The most famous of open water polynyas was recorded in the Eastern Weddell sea during the winters of 1974, 1975 and 1976. An area of $2-3 \times 10^5$ km² of open water remained in the

same location for several months each winter [Zwally & Gloersen, 1977].

These patches of open water are estimated to cover 5% of the total area in the Weddell Sea, exerting a significant influence on the presence of fogs in coastal Antarctica. Winter fog events, around Halley, are thought to be due to the presence of polynyas near the Brunt Ice Shelf coast [Anderson, 1993].

1.6 Aims of this Thesis

The aims of this thesis are to increase our understanding of aerosol sources, and deposition processes, to the snow. The ultimate aim is to enable more accurate interpretation of ice core data, thus allowing derivation of past atmospheric concentrations.

The structure of this thesis is as follows. **Chapter 2** deals with the sampling techniques and analytical procedures used throughout this work. A large number of samples were analysed for this project and the length and detail of chapter 2 reflects the work involved. **Chapter 3** attempts to identify the aerosol sources for the chemical species studied, (sea salt, methanesulphonic acid (MSA) and non sea salt sulphate). Meteorological data from Halley are used to determine whether the aerosol sources are local ones. Longer range air mass origins, (back trajectories) are then used to reinforce the aerosol sources suggested. **Chapter 4** takes a general look at the similarities and differences between the aerosol and snow record at Halley. Comparisons are also made to the other bases involved in the collaborative project. **Chapter 5** looks at the processes that control aerosol deposition in

coastal Antarctica. The effects of wet, dry and fog deposition, sublimation, wind pumping and drifting and blowing snow are examined using experimental data and theoretical models. Finally, the contribution each process makes to aerosol deposition is quantified. **Chapter 6** looks at the accumulated snow record at Halley in comparison with shallow firn cores also drilled at Halley. **Chapter 7** summarises the conclusions and implications of this thesis and makes detailed recommendations for possible future lines of investigation.

Figure 1.1: General map of Antarctica, showing significant ice core drillings and sites of continuous aerosol measurements.

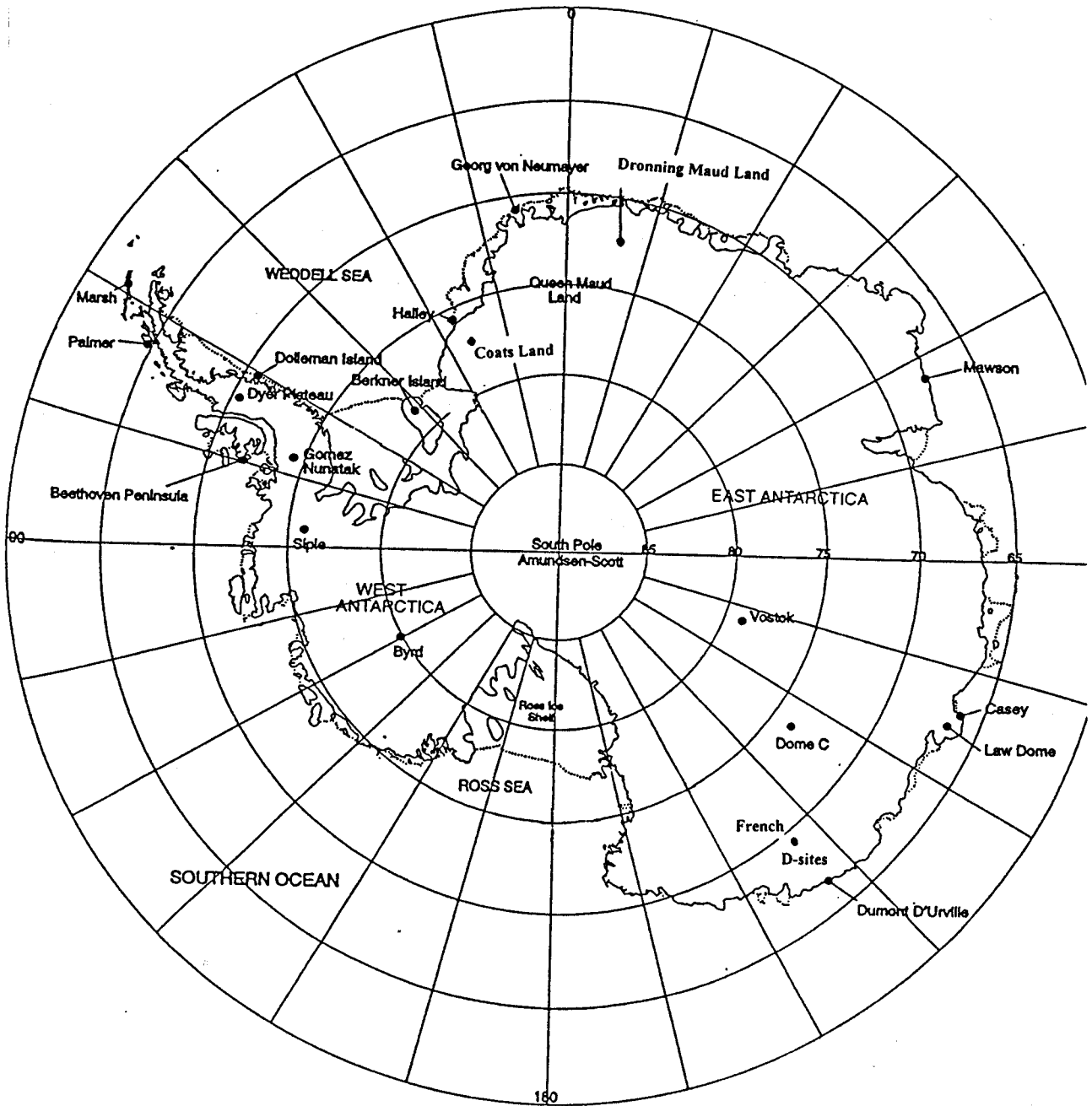


Figure 1.2: *Position of the three bases involved in the collaborative sampling programme.*

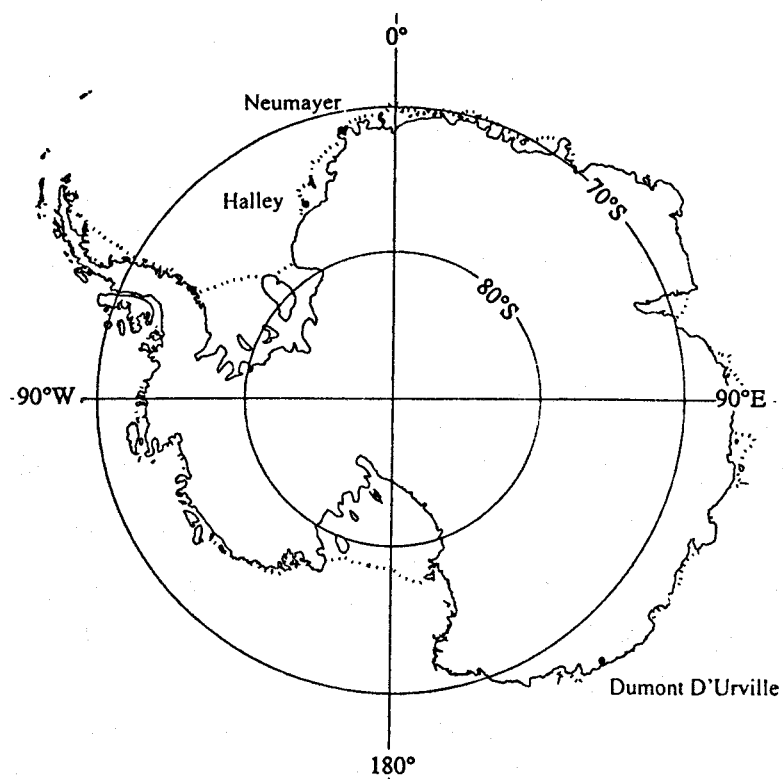


Figure 1.3: A sketch map of the Brunt Ice Shelf in the Halley region. (Approximate contours shown in metres.)

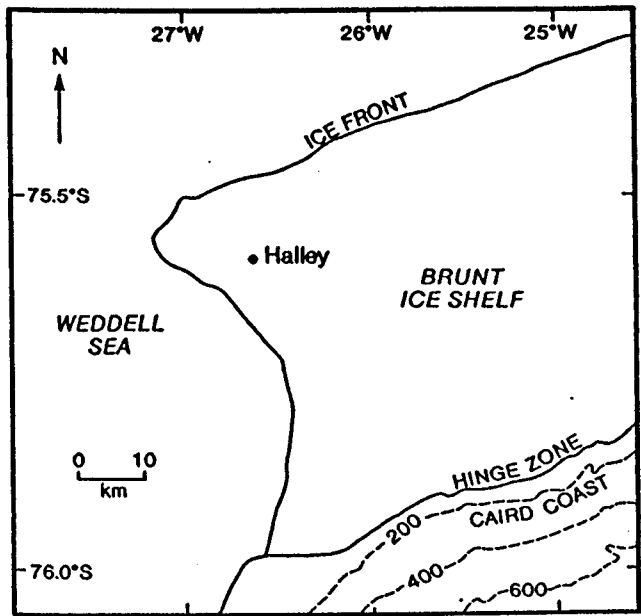


Figure 1.4: Mean monthly temperatures at Halley, Jan 1991 - Feb 1993.

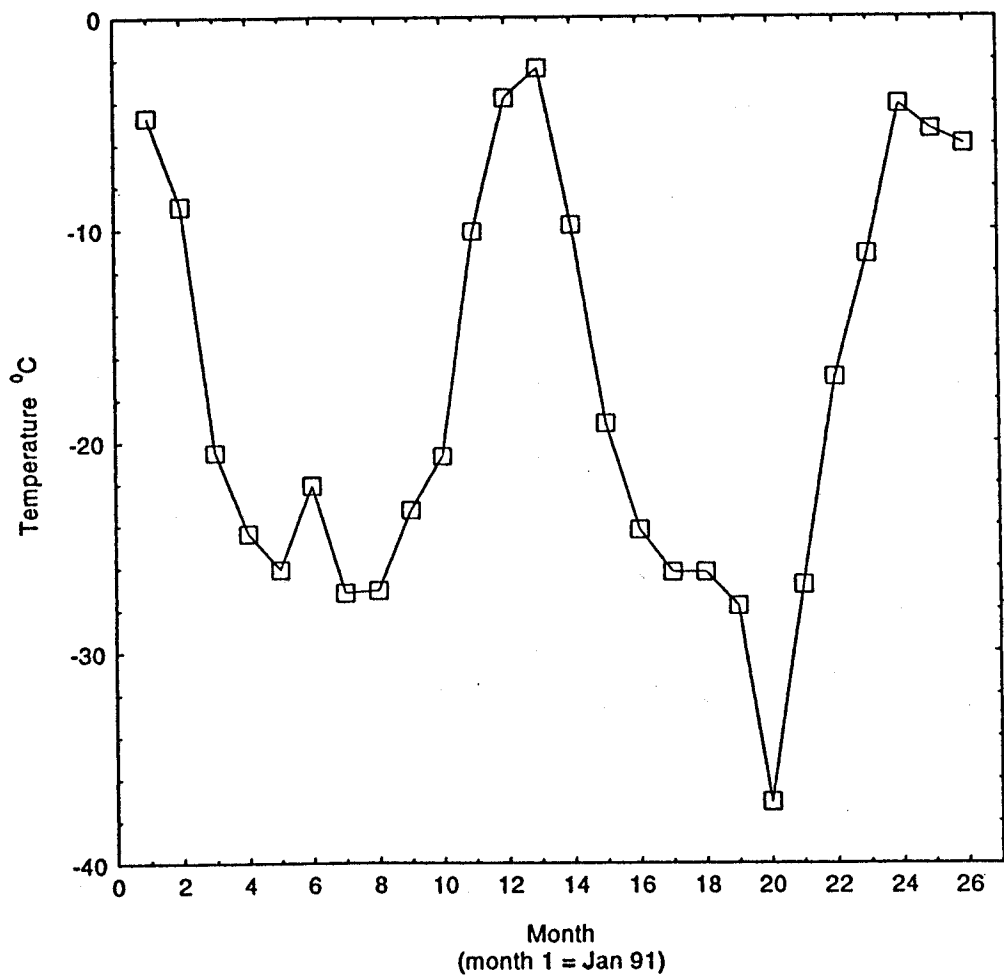
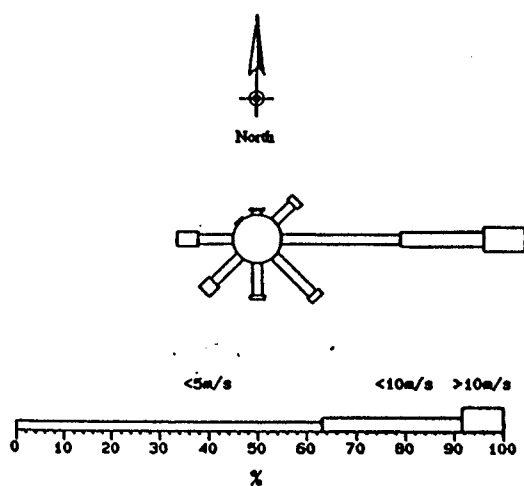


Figure 1.5: Typical wind rose for Halley [King, 1989].



Chapter 2

Sample Collection and Analytical Techniques

2.1 Introduction

The aim of this chapter is to provide information on the samples collected for this project and the analytical methods used to extract the data. The project will concentrate on results from Halley, but with useful comparisons drawn from the other two coastal sites.

2.2 Aerosol Sampling at the British Antarctic Survey

The British Antarctic Survey (BAS) have contributed to aerosol collection throughout the years, but have only recently undertaken a continuous, year round programme. However, the importance of better understanding our knowledge of the air-snow relationship is not a new one to BAS. Initial work carried out by Dick, [1990] and Peel & Wolff, [1982] on the Antarctic Peninsula, investigated the link between concentrations of heavy metals and major cations in air and snow. A snow pit and shallow firn core were sampled concurrently with an aerosol programme, to identify the link between air-snow concentrations.

The aerosol samples were collected on 37 mm diameter, Millipore, 0.45 μm pore size, mixed cellulose acetate and nitrate filters, supplied in disposable styrene holders. The holders were mounted face downwards, inside heavy-duty polypropylene jars, to protect the filter face from blockages by falling, or blowing snow. Although this project spanned just a few months, the filter type used was found to be successful in sampling aerosol material, and the jars adequately protected the filter faces.

2.3 Rationale for the Sampling Protocol at Halley, for this Thesis

The success of the sampling techniques employed on the Peninsula by Dick, [1990] and Peel & Wolff [1982], made selection of the filter type and aerosol sampling set-up for the year round programme easy. The mixed cellulose ester filters were found to be easy to handle and clean. The same filters and sampling techniques were therefore chosen for the collection of aerosol particles for this thesis, which is part of the collaborative project described in section 1.4.

Aerosol and snow samples were collected from British Antarctic Station, Halley, during a period of two years. Halley is a coastal location, situated on the Brunt Ice Shelf, 14 km from the Weddell Sea (see chapter 1), and was chosen for the aerosol and snow sampling because it is continually manned throughout the year, with scientific personnel. The samples studied for this project are outlined here:

2.3.a Samples Collected

- 1 Daily filters, collecting aerosol particulate matter.
- 2 Surface snow and freshly fallen, accumulated snow samples.
- 3 Weekly filters collecting both aerosol and gaseous phase material.
- 4 Two, 2m firn cores collected after the first year of aerosol sampling and covering one year of surface snow and aerosol collection.
- 5 One, 2m firn core collected after completion of the two year sampling project, and therefore covering the complete time span of the project.

The rationale behind **daily** aerosol and snow sampling was to obtain the most representative aerosol and snow concentration for each day possible. With such a record, individual events in the data set can be studied, together with specific meteorological conditions. This is essential if the aerosol sources are to be determined, as high concentration events (the key to pin-pointing the most likely aerosol origin) will need to be easily identified. A longer aerosol sampling period would probably smooth out daily fluctuations. Daily snow collections are necessary if individual snowfalls are to be identified, and the concentrations for each snowfall determined. An accumulated snow record collected daily, over the year, can then be used to see how well snow concentrations are preserved in firn cores. Without daily snow sampling, a snowfall event could easily be missed.

All samples were analysed for the major ions: chloride, nitrate, sulphate, methanesulphonic acid (MSA), sodium, magnesium, potassium and calcium. The main species of interest here, are sea salt (determined from sodium data), non sea salt sulphate (see section 3.8.d) and MSA. The analytical techniques used are described in detail in section 2.14.

2.4 The Aerosol Record

Two methods of filter collection were undertaken for this study. A daily aerosol record was collected from February 1991 to 1993, on mixed cellulose ester filters. A weekly record was also obtained throughout February 1992 to January 1993, using teflon/nylon combination filters, with the teflon filter exposed to the air first. Teflon filters collect the aerosol component, whilst two successive nylon filters trap acidic gases.

Table 2.1: Dates of when and how filters were treated.

	Cleaned	Collected	Storage	Extraction	Analysis	
					Anion	Cation
Daily Aerosol 1991	1990	Halley 4 Feb 91 - Jan 92	-20°C	1994	1994/95	1995
Daily Aerosol 1992	1991	Halley 5 Feb 92 - Jan 93	-20°C	1995	1996	1996
Weekly Teflon	1991	Halley 5 Feb 92 - Jan 93	-20°C	1996	1996	-
Weekly Nylon	1991	Halley 5 Feb 92 - Jan 93	-20°C	1995	1995	-

2.4.a Cleaning Procedures

2.4.a(i) Daily Aerosol Record

Aerosol phase particles were collected using Nucleopore MF 37 mm, 0.8 μm filters of mixed cellulose ester. (Manufacturers suggested filter uptake, >99.99% of total aerosol mass in a typical marine atmosphere). These were cleaned in batches of 50 in polyethylene

bottles, undergoing a series of five ultra high purity (18 M Ω) water rinses. This included agitation in an ultrasonic bath and an overnight stand. The filters were left to dry in a class 100 clean room, on their housing units and support pads. The cleaned units were then individually bagged for transport to Antarctica. The filter holders and bags had also undergone successive ultra high purity water cleans and the filter support pads were cleaned in the same way as the filters themselves.

2.4.a(ii) Weekly Aerosol Record

Particulate matter was collected on Gelman Zefluor (teflon) 37 mm diameter, 1 μ m pore size filters, on a weekly basis. These teflon filters were cleaned in batches of 20, 25 and 28 in polyethylene bottles. A mixture of 18 M Ω water and Aristar 99.9% methanol was used in two rinses, followed by a lone methanol rinse to ensure wetting of the filters. Three final overnight water rinses and a ten minute agitation in a ultrasonic bath, completed the cleaning process.

Gaseous material was sampled using Gelman Nylasorb (nylon) 37 mm, 1 μ m filters. These nylon filters underwent a similar cleaning process as the teflon filters, however the methanol was replaced with 1.8 mM carbonate/1.7 mM bicarbonate eluent for more efficient cleaning of the nylon filters.

Porous polyethylene support pads were cleaned by following a series of ultra high purity water rinses and an overnight soak, as were the housing units. Each filter was dried on the

support pad and housing unit.

Table 2.2: Manufacturers details of filters used

1991 - Daily	Description	Part Number
Filters	Nucleopore Mixed Cellulose 37 mm diameter, 0.8 μ m pore size Porosity 70-88%	140809
Support Pads	Nucleopore Polyethylene	220800
Holders	Nuclepore 3-piece Styrene Acrylonitrile 37 mm diameter	300045
1992 - Daily		
Filters	as 1991	
Support Pads	as 1991	
Holders	Gelman 3-Piece Unit 37 mm diameter	4339
Weekly		
Filters	Gelman Nylasorb, 37 mm diameter Gelman Zefluor, 37 mm diameter 1 μ m pore size, Porosity 70-85%	66508 P5PL037
Support Pads	as 1991	
Holders	as 1991	

2.4.b Sampling Procedure

The 1991 aerosol collection programme took place at Halley 4 (75°36'S, 26°48'W). Throughout 1992/93, after the station was decommissioned, the programme was continued at Halley 5 approximately 14 km away (75°35'S, 26°19'W) (see figure 2.1). Specifically, daily filters only, were collected from 3 February 1991 - 20 January 1992, at Halley 4. At Halley 5, daily and also weekly filters were then collected from 12 February

1992 - 31 January 1993. The collection of aerosol samples was undertaken by the wintering meteorologists at Halley.

To eliminate uncertainties, due to the relocation of the sampling site, the collection set-up at each station was kept as similar as possible. Each system consisted of mains power, drawn from inside the 'Ozone Caboose' at Halley 4, and the 'ICB' (ice and climate building) at Halley 5 (see figure 2.2). A vacuum pump, flow rate monitor and air volume meter were also housed in the same locations.

Silicone tubing, fixed onto catenary lines, was used to connect the filter inlet to the pump. A two way tap in the silicone tubing allowed, if necessary, the pumping of two filters simultaneously. The filters themselves were located in downward pointing cylinders, to protect their face from blockages due to blowing snow. The cylinders were attached to 3 m nylon poles, simply pushed into the snow. Figure 2.3 shows a schematic reconstruction of the filter sampling set-up.

A total of three filter cylinders could be attached to the nylon pole: one filter unit acted as a field blank and was not connected to the pump, and the other two cylinders were used to collect either daily or weekly samples. These two filter cylinders were connected to one pump via the two-way tap already mentioned. At both sampling stations, the filters were positioned about 300-400 m in a generally upwind direction from any generators and the area kept free from vehicle movement.

The filter housing units were assembled so that the filter face was protected by a covering section. The unit could then be inserted into the protective cylinders and connected to the silicone tubing, without the filter face becoming exposed. On completion, the covering section was removed and pumping began, without risk of contamination.

The filters were removed in much the same way, by replacing the protective covering section and double bagging the units in pre-cleaned bags. The meteorologists wore clean, shoulder length polyethylene gloves whenever handling the filter units. Once removed, the filters were stored in water-tight boxes below the snow surface, where the temperature did not exceed 0°C, until they could be returned as frozen cargo, to Cambridge for analysis.

Throughout the sampling period, an additional monthly filter, not connected to a pump, was also collected after a days exposure. This filter acted as a control and can give information on any possible passive sampling . Herein, this will be referred to as a **field blank** (see section 2.7).

2.5 Volume of Air Pumped

Air was sucked, or vacuum pumped, through the 1991 daily filters at a rate of approximately 20 L per minute. This meant that a typical daily filter sampled 32 m³ of air, with a sampling face velocity of 31 cm s⁻¹ for the 37 mm filters. Occasionally, during bad weather, the filters were left on for longer than one day, but as the volume of air was always recorded this could be accounted for.

Between February 1992 and January 1993, at Halley 5, weekly and daily filters were run simultaneously. The volume of air pumped through the two filter units was controlled by a two-way valve in the silicone tubing. This valve should have split the volume of air equally between the daily and weekly filter units. However, on analysis, it was found that very little aerosol material was trapped on the weekly filters. The average concentration was only 25 ngm^{-3} for chloride and 13 ngm^{-3} for sulphate, compared to the daily filter averages of 110 ngm^{-3} chloride and 60 ngm^{-3} sulphate. These very low weekly values seem to suggest that either the valve was not functioning, or it was set incorrectly.

2.5.a Two-way Valve Set-up

In order to try and re-create the conditions at Halley which caused this problem, the sampling set-up was simulated in the laboratory. Four hypothesis are put forward for test,

• to explain the very low concentrations on the weekly filters. These were:

- 1 The original two way valve was incorrectly set-up (Figure 2.4b).
- 2 A break in the silicone tubing occurred in the weekly filter line.
- 3 The teflon, nylon, nylon, weekly filter units created a greater resistance to air being vacuum pumped through the unit (Figure 2.4a).
- 4 Particles were knocked off the weekly filters after collection.

2.5.a(i) Results and Discussion of Hypothesis

As there is no reported evidence of aerosol material being removed or knocked off a filter

surface after collection, hypothesis 4 seems very unlikely and is disregarded. Hypothesis 3 was tested in the laboratory, with the filter set-up shown schematically in figure 2.4a. The two filter units gave equal flow rates on the meter, showing that the resistance was not significantly greater through the teflon, nylon, nylon (TNN) unit. Also, the porosity of the two types of filter units (daily and weekly), is the same (see table 2.2). Hypothesis 2 was tested by disconnecting the tubing from the TNN unit to the two way valve. This resulted in 0% of air flow through the daily sample due to its higher resistance. Only hypothesis 1 (Figure 2.4b) gave 100% flow through the daily filter and 0% flow through the weekly unit. This indicates that the original set-up was probably incorrect and dual flow was not occurring through the two-way tap. This could only have been the result of incorrect setting of the valve. The weekly filters were therefore isolated from the pump and not sampled. This means that the volume of air through the 1992 daily filters was 32 m³ per day and through the weekly TNN units, 0 m³ per day.

As a result, the weekly filters are now disregarded from the dataset, as they do not contain the information they were intended to collect. The daily filter record, does however, contain meaningful data which will be used for this project. Finally, in retrospect, it may have been very difficult to confidently determine the volume of air sampled by the weekly filters, had the two-way tap been set correctly, unless a flow meter was attached to each line.

2.6 Extraction of the Aerosol Phase

The daily aerosol record was obtained by individual extraction of the aerosol matter on the filters. All the work was carried out in a class 100 clean room, close to the face of HEPA filters supplying air to the laboratory, and whilst wearing full surgical clothing. The filters were carefully removed from their holders using stainless steel tweezers. The tweezers had previously been cleaned in ultra high purity (UHP), water and soaked in an ultrasonic bath. The filters were then placed in 30 ml polyethylene bottles, which had undergone successive soaks in UHP water baths. 8 ml of UHP water were added using a pipette and the sealed bottles submerged, upright in a ultrasonic bath. They were left agitating in this manner for one hour. The extraction liquid was then decanted off and stored in pre-cleaned 10 ml vials. The extract was stored at -20°C until analysis. For 50 of the filters this process was repeated, to determine how complete the first extraction had been.

An additional **analytical blank** (see section 2.7) was also introduced at this stage. The analytical blank underwent the same extraction process as the actual samples, but without a filter being present and is simply ultra high purity water.

The method of extraction was chosen after experimenting with different amounts of leaching liquid and varying the length of time in the ultrasonic bath. The above conditions were found to be the optimum for both extraction efficiency and speed. Initially, 4 mls of UHP water were used to extract the aerosols from the filters, with 1 minute in an ultra sonic bath and 15 minutes standing time. However, the extracted, or leached liquid was found to contain concentrations low enough to be indistinguishable from the field blank (see section 2.7), demonstrating the inadequacy of the extraction process. As a result, the length

of sonication was increased to 15 minutes. This in fact, did not improve the extraction and the leached liquid still displayed random values and a similarity to the field blank. The length of sonication was finally increased to 60 minutes and the amount of leaching water increased to 8 mls, to provide a larger archival sample and a greater extraction efficiency.

2.6.a Extraction Efficiency

To study the efficiency of the first extraction at removal of trapped aerosol particles, two leachings were carried out on 50 filters. The extraction efficiency can be expressed graphically (Figure 2.5), using a linear least squares regression, forced through zero. For chloride, this gives 95% efficiency of removal of particles from the first filter. However, experiment shows that between 1 and 10% of the water used to extract the aerosols is actually left behind on the filter face, implying that the extraction efficiency is closer to 100% for chloride. Sulphate gives a similar result with the regression showing 94% efficiency. Once again we can assume this to be 100%, after considering the amount of liquid left behind. For both chloride and sulphate, it is therefore not necessary to make a correction for the efficiency of extraction.

The regression curve for methanesulphonic acid is harder to interpret. The majority of filters used to examine the efficiency were those sampled during the winter, when values for MSA were low. Figure 2.5 shows an efficiency as low as 84% for MSA, but by selecting summer filters, with concentrations significantly higher than the detection limits, it is possible to see that this value could be closer to 90% and perhaps higher. Assuming

that these major anionic species must, theoretically, be extracted in the same way and that there is no evidence in the literature to suggest MSA 'sticks' to the filter surface more than any other species, we must assume that the extraction efficiency for MSA is also 100%, (after having taken into account the amount of leaching liquid remaining on the filter). Therefore, no extraction correction will be made for this species.

The extraction efficiency for sodium is 90%, shown graphically in figure 2.5. For magnesium, there is more scatter, but this could be accounted for by the high field blank, (see section 2.7 and table 2.3), and that the values for the second extraction are not only very low, but close to the detection limit. Even with this scatter, the efficiency is again 90%. Once again, the amount of extraction liquid left behind on the filter leads us to assume 100% extraction efficiency for sodium and magnesium, therefore, no correction is made to the data. Similar results are found for potassium and calcium, the other major cations studied.

Other researchers have also found 100% extraction efficiency from filters. Ducroz, [1996] found that once 100 μL of water left behind on the filter was accounted for, the extraction efficiency for major anions, including MSA, and cations was indeed 100%.

2.7 Filter Blanks

Controls, or filter blanks, were introduced throughout the cleaning, sampling, extraction and analysis stages of this project.

2.7.a Test Filters

Initial **test filters**, cleaned in much the same manner, and at the same time as the **real filters**, were intended to ensure the effectiveness of the filter preparation procedure (see section 2.4.a(i)). However, unlike the real filters which were cleaned in batches, the test filters were cleaned individually [Wolff, personal communication]. This provided extremely low concentrations (chloride 0-44 ng g⁻¹, nitrate 0-8 ng g⁻¹, sulphate 0-59 ng g⁻¹), and the cleaning process was judged to be sufficient. (NB: The blank values quoted are in ng g⁻¹ in solution and not per g of filter). However, due to the large number of filters needing to be prepared, individual washing was not undertaken for the real filters. Instead, these were washed in batches of 50. This resulted in an unsatisfactory level of ions being left behind on the filter face as can be seen from the high field blank values (Table 2.3).

2.7.b Field Blanks

Throughout the sampling campaign, an additional monthly filter, not connected to the vacuum pump was also collected, after an exposure time of 24 hours. This filter, known as a **field blank**, acts as a control and can give information on the possible effects of passive sampling. Apart from not being vacuum pumped, filter field blanks underwent identical processes of preparation and analysis, to the real filters. By subtracting this field blank value from the chemical concentration found on actual filters, a meaningful value for the chemical concentration of particular aerosol species can be found.

The concentrations determined, by ion chromatography, for the filter field blanks are shown in table 2.3. All the field blank values are high, with a large degree of uncertainty. Consequently, after these values are subtracted from the aerosol concentration found on the real filters, (field blank values in table 2.3 must firstly be converted into ng, by multiplication of the volume of extraction liquid used to remove the aerosols), some negative numbers appear in the final aerosol data set. This reflects the highly variable field blank values, due to the incomplete cleaning of the filters. High field blank values are also associated with the relatively poor detection limits (see later), possibly as a result of the low air volumes.

Table 2.3: Field blank values (Outliers removed if \geq twice the standard deviation, plus the average value, of the data set [Miller & Miller, 1993].

	Field Blank Concentration (ng g ⁻¹)								
	MSA ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺	NH ₄ ⁺
1991 Daily Filters	5	35	483	56	15	8	n/a	n/a	n/a
Standard Deviation	±3	±13	±180	±24	±15	±8			
No.of Outliers Removed	1/18	1/18	0/18	0/18	1/18	3/18			
1992 Daily Filters	15	59	650	36	24	4	14	8	258
Standard Deviation	±6	±20	±208	±12	±16	±2	±3	±6	±48
No.of Outliers Removed	0/11	1/11	0/11	1/11	0/11	1/11	1/11	1/11	0/6

Table 2.3 shows that the field blank for nitrate is the worst affected, with values of 650 ng g⁻¹ ±208 ng g⁻¹). Filters direct from the manufacturers box, give values in the region of 500 ng g⁻¹, implying that the cleaning process was actually adding nitrate onto the filters. Tests were also carried out on real filters which were never exposed to the Antarctica air. These ‘spare’, real filters also gave particularly high nitrate concentrations (405 ng g⁻¹ ±130 ng

g⁻¹). This implies that the cleaning process, rather than passive aerosol sampling, is the cause of the high nitrate loadings. Furthermore, experimental tests suggest that nitrate concentrations extracted from cleaned, wet filters, were substantially lower than this value. It is therefore possible that uptake occurred during the drying process. It seems the filters may have inadvertently been exposed to fumes from two nitric acid cleaning baths, which at the time, were being stored in a fume cupboard, in the same laboratory [Wolff, personal communication]. The long storage time between cleaning, collection and analysis may also have created a problem, (filters were cleaned in early 1990 and analysed in 1994/95 - see table 2.1). As a result of the extremely high field blank value, nitrate data have on the whole been ignored from this project.

2.7.c Analytical Blanks

The **analytical blank** is ultra high purity water that undergoes the same extraction and analytical process as the actual samples, but without ever coming in contact with a filter. The values for the analytical blanks are shown in table 2.4. This ultra high purity water (18 MΩ) underwent identical laboratory processes as the filter extractions themselves and demonstrates that the contamination problem lies with the field blanks and not the analysis, or extraction procedures.

Table 2.4: Analytical blank values NB: Outliers removed if \geq twice the standard deviation, plus the average value, of the data set. [Miller & Miller, 1993]

* < the detection limit

	Analytical Blank Concentration ng g ⁻¹								
	MSA ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺	NH ₄ ⁺
1991 Daily Filters	<1	7	8	13	3	3	n/a	n/a	n/a
Standard Deviation	*	±3	±3	±8	±3	±4			
No.of Outliers Removed	0/31	1/31	1/31	1/31	0/31	0/31			
1992 Daily Filters	<1	5	20	10	7	3	7	2	0.6
Standard Deviation	*	±4	±25	±6	±12	±3	±4	±2	±1.4
No.of Outliers Removed	0/76	0/76	0/76	2/76	3/74	4/74	4/74	4/74	1/12

2.7.d Filter Detection Limits

The analytical detection limits are calculated based on twice the standard deviation of the field blank [Miller & Miller, 1993]. As the field blank includes all stages of a filter's 'life', a detection limit based on this, gives an accurate representation of our procedural limitations. Table 2.5 shows the determined values, with limits for all species being less than 10% of the total, average concentration on the filters. The high limits, for species such as sulphate and chloride, once more explain the negative numbers obtained in the final data set fairly well.

Table 2.5: Filter detection limits

	Filter Detection Limits ng m ⁻³								
	MSA ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺	NH ₄ ⁺
1991 Daily Filters	1	6	*	11	4	1	**	**	**
1992 Daily Filters	3	10	*	6	8	1	1	3	22

* not included in thesis

** these ions were not analysed in 1991

2.8 Local Contamination of Filters

Despite the presence of two generators at Halley base, there seems to be little, or no effect from local pollution. Wolff and Cachier [In press] used an aethalometer to measure black carbon in the air at Halley, by measuring the attenuation of light from a light beam, on being passed through a filter. They found the black carbon data set to be dominated by large spikes. By classifying the site and data according to wind speed and wind direction, it was determined that large black carbon spikes were associated with winds blowing from the station generators, towards the aethalometer inlet. However, they also found that MSA, sulphate and chloride values (for the same time period and location as the 1992 daily aerosol collection programme) were unaffected by even the very largest of these black carbon events. Even the highest event, recorded over a 4 year period, did not have an affect on anionic concentrations; the concentrations were unperturbed to 5ng m^{-3} uncertainty. From this evidence we can safely assume that the contribution from the base, to the content of aerosol species on the filters, is minimal.

2.9 The Snow Record

For this study, two types of snow samples were collected: surface and accumulated samples. Surface samples collected the top 15 mm of snow, on a daily basis. Accumulated samples collected freshly fallen snow, whenever a significant increase was measured on an accumulation stick. This project ran concurrently with the aerosol programme, throughout

July 1990 to February 1993.

2.9.a Cleaning Procedures

All the bottles used for sample collection were cleaned in a class 100 clean room. They were initially soaked in ultrasonic baths, containing ultra high purity water, (18 MΩ) and a small amount of Aristar grade methanol. This was followed by three successive rinses in ultra high purity water only. The bottles were then packed in foam racks and placed in two, sealed polyethylene bags, ready for transport to the Antarctic.

2.9.b Sampling Procedure

The snow sampling programme ran from 4 July 1990 to December 1991, at Halley 4 (75°36'S, 26°48'W). Following the decommissioning of this base in December 1991, the project moved to Halley 5 (75°35', 26°19'W), where it ran until 01 February 1993. The collection at Halley 4 occurred approximately 200 m south of the base and at Halley 5, within the base perimeter, just a few metres south of one of the science platforms (see figure 2.2). The sampling sites were designated clean areas, entered only by personnel wearing clean room hoods and shoulder length gloves. Vehicle activity was also kept to a minimum around this area. As the sites were situated to the south of both bases, the predominantly easterly winds kept contamination to a minimum (see section 2.8). Each day, new samples were collected by advancing upwind within the clean area, eventually starting again to one side of the original point.

2.9.b(i) Surface Snow

Surface snow was collected on a daily basis, using a specially designed device (Figure 2.6). Two aluminium skis skimmed the snow surface, whilst two 9 ml bottles sampled the snow in between the runners themselves. One bottle collected the top 10 mm, whilst the second sampled 3-15 mm below the surface. Allowing for naturally undulating surfaces at least 10 mm of sample would be obtained each time. The uppermost sample was called **s1** and the bottom, **s2**.

2.9.b(ii) Accumulated Snow

The second sample type, accumulated snow samples, were collected whenever a significant increase in snow surface height (> 1.5 cm) occurred against an accumulation stick. After a snowfall event, or any increase in accumulation occurred, a shallow pit was dug using a spade previously rinsed in the UK, in ultra high purity water. This created a vertical surface from which to sample. The sampling device consisted of a plastic holder with vertically overlapping holes, into which pre-cleaned 30 ml bottles were inserted (Figure 2.7). This sampler was simply pushed into the fresh accumulated wall of snow. A maximum of 12 samples could be collected, at any one time, depending on the amount of accumulation which had occurred. The uppermost surface sample is labelled **w1** and the deepest, **w12**. Table 2.6 shows the depths to which the accumulated snow sampler could reach. This collection method enabled snowfall events to be monitored and profiled completely.

Table 2.6: Depths from which accumulated snow samples were taken.

Accumulated Snow	w1	w2	w3	w4	w5	w6	w7	w8	w9	w10	w11	w12
Top (mm)	2.5	18	34	50	66	82	98	114	130	146	162	178
Middle (mm)	15	31	47	63	79	95	111	127	143	159	175	191
Bottom (mm)	27	43	59	75	91	107	123	139	155	171	187	203

Each time a sample was collected, a series of observations was made. These included wind speed and direction, temperature, accumulation (measured against an accumulation stake since the previous sample), time, significant weather and any other comments. Comments included any base activities which might affect the samples. On days when the wind speed exceeded 30 knots, samples were not usually taken.

The collected samples were kept frozen at all times and sent back in a deep freeze at -20°C, for analysis in Cambridge. Samples were melted when required for analysis and the remaining liquid re-frozen and kept as an archive sample.

2.10 Detection Limits and Snow Blanks

For the 1991 anionic species, depending on the method of analysis, the detection limit was estimated at 0.5 ng g⁻¹ and determined experimentally [Pasteur, personal communication]. However, in reality, it is likely that this is an underestimation of the actual detection limit for all species. Table 2.7 shows that for 1991 and 1992 cations the detection limits were higher, based on twice the standard deviation of a blank value [Miller & Miller, 1993]. The analytical blank was ultra high purity water, 18 MΩ, which underwent identical analytical

processes as the snow samples themselves. The average analytical blank value for MSA was 0.5 ng g^{-1} , chloride $2 \text{ ng g}^{-1} \pm 1$, nitrate $3 \text{ ng g}^{-1} \pm 3$, sulphate $3 \text{ ng g}^{-1} \pm 2$, sodium $2 \text{ ng g}^{-1} \pm 3$, magnesium $4 \text{ ng g}^{-1} \pm 2$, and for potassium $1 \text{ ng g}^{-1} \pm 2$.

Table 2.7: Snow Sample Detection Limits

ng g^{-1}	MSA	Cl^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	K^+
1991	$\approx 0.5^*$				5	5	4
1992	0	2	6	4	5	5	4
No. of outliers removed	0/40	3/40	3/40	2/40	0/33	3/33	0/33

* Detection limit determined experimentally, no outliers removed, and probably an underestimation of the actual limit

2.11 Other Snow Samples

Other types of snow samples, other than freshly fallen snow and daily collections of surface snow, were also collected. These included samples of rime, drifting and wind pumped snow. However, as we shall see later in this thesis, it is extremely difficult to distinguish between the different types of snow samples.

2.11.a Drifting Snow

In order to investigate how drifting snow affects the spatial variability of the chemistry of surface snow and ultimately that which is seen in ice cores, samples of drifting snow were collected.

An array of nine, $1 \text{ m} \times 6 \text{ mm}$ nylon rods were laid out perpendicular (N-S) to the main

wind direction (easterly) in a clean area of snow. The stakes were positioned at spacings of 0, 5 cm, 5 cm, 20 cm, 20 cm, 2 m, 2 m, 20 m, 20 m apart and pushed at least halfway into the snow. The stakes were numbered 1-9, with stake 1 being the most northerly and stake 9, the most southerly. The height of each stake above the snow surface was also measured.

Three sampling campaigns were initiated during March, July and September 1993, with samples collected after each significant drift event. Surface snow was collected, using the upper collection tube of the device shown in figure 2.6 and the height of the stake above the snow surface was remeasured. Care was taken to avoid unnecessary contact with the sampling area.

The results of this experiment are described in section 4.10.

2.11.b Sastrugi - Wind Pumping

Undulations in the snow surface, caused by the depositional and erosional characteristics of wind are known as sastrugi, (see section 5.6). The presence of these features is thought to affect the chemical concentration of snow in some parts of Antarctica, due to the effect of wind pumping. The chemistry of upwind faces of individual sastrugi are thought to become more concentrated, as snow filters out aerosol particles from air passing through it [Harder, 1996; Waddington et al., 1996].

To investigate the extent to which this affects coastal Antarctica, sastrugi samples were collected on various faces of six features in January 1995, at a clean site near Halley research base. Collections were made from the front face of each sastruga, at the top and bottom, taken from each side and also from the tail (see figure 2.8). Samples were collected in pre-cleaned bottles and sampled from a undisturbed area of snow. The surrounding topography was also noted.

Results of this experiment are described in section 5.6.

2.11.c Rime Samples

Rime forms when supercooled liquid droplets attach themselves to snowflakes and freeze on contact, acting as nuclei for snow crystals to grow on. Rime also commonly forms on the snow surface. As this is an alternate, yet potentially important processes for deposition of particles, samples of rime were collected from a site on the Dyer Plateau, on the Antarctic Peninsula, (70°S40.25', 64°W53.1', altitude 2008 m).

Samples were collected directly into pre-cleaned sample vials by scraping from either the surface snow pack, or from clean nylon strings tied horizontally between two bamboo poles, using a pre-cleaned scalpel. Eight samples were collected at the following heights:

A and B - string, height 0.25 m above snow surface
C and D - string, height 0.80 m
E and F - string, height 1.10 m
G and H - surface snow

Results of this experiment are described in section 5.10.b(i).

2.12 The Firn Core Record

For this study three, 2 m firn cores were drilled. Core 1, was drilled at Halley 5 at the end of the sampling programme and covered the entire collection period. Core 2 was collected at Halley 4 and core 3 at Halley 5. Both these later cores were drilled at the end of the first year of snow and aerosol sampling, February 1992. They therefore contain a record of snow which fell over the previous year (1991-1992). The firn cores offer the opportunity to study any post depositional changes in the ice, as well as direct comparison of an ice core with the chemical changes in the atmosphere. Cores 2 and 3 also allow comment on the spatial variability of the two sites. Results of this experiment are described throughout chapter 6.

2.12.a Drilling of the Firn Cores

An aluminium hand auger drill was used for these cores. This drill is capable of reaching up to 10 m in depth. The drill barrel itself is 1 m long and additional 1 m rods can be attached to the top of the drill to extend it. The drill is rotated by hand, using a t-bar at the top of the assembly. Up to 1 m core sections are broken when the drill can no longer rotate, indicating that the barrel is full of core and chippings. To break the core at this point, the t-bar is rotated back and forth to enable the sharp core dogs, on springs, to dig into the firn.

This breaks the core and enables removal from the borehole.

The cores are then packaged in polyethylene sleeving and cardboard outer tubes. The top of the core is clearly labelled on the packaging. These are stored at -20°C , in insulated boxes and transported back to Cambridge as frozen stowage.

2.12.b Sub-sampling of the Firn Cores

The cores are sub-sampled at -15°C , in a cold room. This process requires two people, dressed in full clean room clothing, including hood and shoulder length gloves. A band saw is used to section the core, after the blade is initially cleaned by cutting an ultra high purity water core ($18\text{ M}\Omega$). Two sections are cut, the first vertically, dividing the core into two halves. One half is kept for archiving purposes and the other sub-sampled further. Horizontal sections are cut, the size of these sections depending on the amount of accumulation a site receives in a year; Halley usually receives about 1 m of snow per year. Each horizontal section has its outside edges removed to obtain the cleanest, most untouched sample possible. These are put into polypropylene melting tubs and melted in a class 100 clean room. The sample is then transferred to polyethylene bottles, and kept frozen until analysis.

2.13 Acknowledgement

Since this project was conceived some years ago a number of people, listed below, have

been involved in the design, collection and analysis of the programme.

Table 2.8: Acknowledgement of Who Prepared and Collected the Samples Available

	Daily Filters	Weekly Filters	Snow Samples	Drifting Snow	Sastrugi	Rime	Firn Cores
Cleaning	E Suttie E Wolff	E Suttie E Wolff	E Suttie	E Wolff	J Hall	R Mulvaney	
Sampling Set-Up	E Suttie	E Suttie	E Suttie	E Wolff	J Hall	R Mulvaney	E Suttie E Wolff
Design	E Wolff	E Wolff	R Mulvaney E Wolff	E Wolff	J Hall	R Mulvaney	
Collection	Winter Met. Team	Winter Met. Team	Winter Met. Team	Winter Met. Team	J Hall	R Mulvaney	Winter Met. Team

2.14 Sample Analysis

Table 2.9: Analysts Involved in this Project

		No. of Samples	Cations	Anions
Daily Aerosols	91	293	Julie Hall	Julie Hall
	92	353	Julie Hall	Julie Hall
Weekly Aerosol				
Teflon:		50	Julie Hall	Julie Hall
Nylon:		100	--	Julie Hall
Snow Samples	91	897	Julie Hall	Elizabeth Pasteur
	92	752	Natalie Holman/ Julie Hall	Julie Hall
Drift	93		Julie Hall	Julie Hall
Sastrugi	95	48	Julie Hall	--
Rime	92	8	Julie Hall	--
Firn Cores	92	400	Julie Hall	Julie Hall

2.14.a Ion Chromatography

A Dionex 2010 ion chromatograph is the principal analytical tool used in this study. The

main species of interest are the anions: chloride, nitrate, sulphate and methanesulphonic acid and the cations: sodium, magnesium, potassium and calcium. These species are chosen as they are the most commonly studied chemicals in an ice core. The sample solution under investigation is injected onto a column, packed with ion exchange resin. This is washed through by a constantly flowing solution, pumped through the column at a fixed rate. Separation of individual species occurs due to differences in the equilibrium distribution of the components between a mobile phase (eluent) and a stationary phase (column packing). The separation involves an exchange process between the mobile phase and exchange groups electrostatically bound to the stationary phase. Components which favour the stationary phase will migrate slower than those having distributions favouring the mobile phase.

As the eluents used for ion chromatography (IC) contain ions in large quantities, they have high and noisy background conductances. As a result of this high background it is difficult to detect the small increase in conductance due to the sample components themselves. To overcome this, the sample passes from the column to a suppressor unit, where the eluent background conductance is chemically reduced to near zero. The sample components are simultaneously converted to their acid or hydroxide forms, giving them higher conductances than the original salt forms.

Depending on the method chosen, flow rate and eluent concentrations, a run takes between 8 and 20 minutes to complete. Concentration is proportional to the area of the sample signal, as a function of time. Standardised, known composition solutions are used to give

a concentration for that sample (see section 2.15).

The machine has been updated over time, resulting in various different column and eluent combinations being used during the course of this study. A summary of the methods used is illustrated in table 2.10.

Table 2.10: Summary of the methods used in ion chromatography

Method	1	2	3	4
Ions	Cl^- , NO_3^- , SO_4^{2-}	MSA^-	MSA^- , Cl^- , NO_3^- , SO_4^{2-}	Na^+ , Mg^{2+} , K^+ , Ca^{2+} , NH_4^+
Separator Column	AS4A-SC	AS4A-SC	AS11	CS12
Eluent	1.7 mM NaHCO_3 / 1.8mM Na_2CO_3	5 mM $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.5 mM-30 mM NaOH	20 mM MSA
Pump	Isocratic	Isocratic	Gradient	Isocratic
Suppressor	Fibre suppressor	Fibre suppressor	ASRS-1 4 mm	CSRS-1 4 mm
Regenerant	50mM H_2SO_4 3ml min ⁻¹	50mM H_2SO_4 5ml min ⁻¹	Recycled eluent	Recycled eluent

2.14.a(i) Method 1:

AS4A-SC Separator Column and Isocratic Pump - Cl^- , NO_3^- , SO_4^{2-}

430 of the 1990/91 surface snow samples were analysed for chloride, nitrate and sulphate using 1.7 mM sodium bicarbonate/1.8 mM sodium carbonate eluent, isocratically pumped in conjunction with the AS4A-SC separator column and AG4-A guard column. A fibre membrane suppressor, with 50 mM H_2SO_4 regenerant, flowing at 3 ml min⁻¹ was also used. For most samples a 200 μl loop was adequate, but for very low concentrations a concentrator column was used. The sample flow rate was 2 ml min⁻¹ and 2 ml of sample

were loaded onto the columns using an autosampler. The data were integrated on a Spectra Physics SP4270.

2.14.a(ii) Method 2:

AS4A-SC Separator Column and Isocratic Pump - F^- , MSA^-

The same 430 snow samples were then analysed for fluoride and methanesulphonic acid using 5 mM of sodium borate eluent, isocratically pumped through the AS4A-SC separator and AG4A guard columns. A fibre membrane suppressor, with 50 mM H_2SO_4 regenerant, flowing at 5 ml min^{-1} was also used. Less than 0.5 ml were hand injected onto the columns. Most samples were run with a $200\text{ }\mu\text{l}$ sample loop, except for very low concentrations.

2.14.a(iii) Method 3:

AS11 Separator Column and Gradient Pump - F^- , MSA^- , Cl^- , NO_3^- , SO_4^{2-}

1992 snow samples and both years of daily aerosol filters were analysed using method 3. The use of the new generation AS11/AG11 columns meant that all of the anionic components could be measured in one run, using a gradient elution technique. An initial eluent concentration of 5 mM NaOH is steadily increased during the run to 30 mM, with a 7 minute eluent run between each sample, to allow re-equilibration to the lower eluent concentration. This method required the eluent to sit under a blanket of helium, preventing contamination by carbonate from atmospheric carbon dioxide. In addition, the eluent passed through an ATC-1 trap column before reaching the load/inject valve or the separator columns to further reduce the carbonate, which can interfere with the sulphate peak. Despite the great care that is taken to prevent the carbonate contamination, a certain amount

still gets onto the column. This small amount does not affected the results obtained and can be seen in the method 3 example chromatogram in figure 2.9. The carbonate peak is number 7.

2.14.a(iv) Method 4:

CS12 Separator Column and Isocratic Pump - Na^+ , Mg^{2+} , K^+ , Ca^{2+} , NH_4^+

1992 daily aerosol filters were analysed for cations using method 4. All cationic species could be studied in one run. CS12 separator and CG12 guard columns were used with 20 mM methanesulphonic acid eluent, isocratically pumped. 0.5 ml of sample were hand injected onto the columns because of the low volumes available and the desire to look at ammonium concentrations. Loading the samples in an autosampler would have increased their risk of contamination from atmospheric ammonium in the laboratory. Recycled eluent was used to suppress the background conductivity. An example chromatogram, using method 4, can be seen in figure 2.10.

2.14.b Atomic Absorption Spectrophotometry

The second analytical tool used in this study is a Pye Unicam SP9 atomic absorption spectrophotometer. In atomic absorption spectrophotometry (AAS), a solution containing small amounts of metallic elements is converted in a flame into a vapour containing 'free' atoms. A light source (hollow cathode lamp) emits radiation which is characteristic of the element under study. This radiation is directed through the vapour and a monochromator isolates the energy of the desired wavelength for the species from neighbouring

wavelengths emitted from the light source. Some of the atoms in the vapour will absorb a proportion of this radiation, resulting in a decrease in the amount of radiation emerging from the vapour. This decrease is measured by a photomultiplier detector.

Sodium and magnesium were analysed using AAS. 1990/91 and 1992 snow samples and 1991 daily aerosol filters were individually hand loaded and run for these two cations. Samples and standards were also acidified to 100 μM , using HCl, to reduce the effect of ionisation contamination.

2.14.c Flame Emission Spectrophotometry

The third and final method of analysis used during this project was flame emission spectrophotometry (FES). The principle of FES is that when an atom, at ground state energy, is excited in a flame to a higher energy level, it emits radiation as it returns to a lower energy level, or to the ground state. The emitted frequencies are characteristic of the atoms of the species under study in the flame and can be detected by a photomultiplier. A monochromator isolates the energy to the desired wavelength in the same way as AAS. As both absorption and emission are due to transition between energy levels of an atom and as these levels are the same whether the transition is up or down, the wavelengths of absorbance or emission are identical.

Potassium is the species under study using FES. 1990/91 and 1992 snow samples were individually hand loaded and run for this cation. Samples and standards were also acidified

to 100 μM to reduce the effect of ionisation contamination.

Table 2.11: Summary of the methods used to analyse the various samples.

	MSA ⁻	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Na ²⁺ , Mg ²⁺	K ⁺	Ca ²⁺	NH ₄ ⁺
1991 Daily Filters	IC Method 3	IC Method 3	AAS	FES	-	-
1992 Daily Filters	IC Method 3	IC Method 3 (also Br ⁻)	IC Method 4	IC Method 4	IC Method 4	IC Method 4
1990/91 Snow Samples	IC Method 2 & 3	IC Method 1 & 3	AAS	FES	-	-
1992 Snow Samples	IC Method 3	IC Method 3 (also Br ⁻)	AAS	FES	-	IC Method 4

2.15 Standards

Two main sets of standardised solutions were used in this study; F-standards and marine standards. The F-standards were made up from Aristar grade solids, dried in an oven before being weighed and made into solution using ultra high purity water, with conductivity less than 18 M Ω . They contain F⁻, MSA⁻, Cl⁻, Br⁻, NO₃⁻ and SO₄²⁻. The marine standards contain Na⁺, K⁺, Mg²⁺ and Ca²⁺. These were made up volumetrically, from Aristar grade chemicals. Ultra high purity water was again used to dilute to the required molarity. NH₄-standards, containing just ammonia were also used where necessary. All the standards were stored in pre-cleaned polyethylene bottles, in a fridge. They were re-made on a minimum of a monthly basis and checked against test spectroscopy grade standards. The ratios of the ions in the standards were chosen to represent typical concentration ratios of the samples themselves (Table 2.12).

Table 2.12: Ratios of the ions in each of the standard solutions

F-Standards	F ⁻	MSA ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻
Ratios of ions	1	1	6	1	1	6
Marine Standards	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺		
Ratios of ions	10	1	1	1		

For ion chromatography, between four and six standards were run at the beginning of an analytical session and used for each calibration. Higher concentration standards were added into the run to allow for any unexpectedly high samples. Water blanks (known as analytical blanks) and standards were inserted at every twelfth sample, to monitor any drift in the peak heights, areas or retention times.

Typical ion chromatography calibration graphs for anions are shown in figure 2.11 and for cations in figure 2.12. The nitrate calibration is also included, even though the contamination on the daily filters have rendered this species void from comment. Figure 2.13 shows a typical atomic absorption spectrophotometry calibration graph for magnesium and sodium and figure 2.14, for potassium using FES.

2.16 Interlaboratory Analytical Tests

A major interlaboratory analytical tests was carried out during this project, for fluoride, chloride and sulphate. Three samples were sent to thirteen participating laboratories in Denmark, Sweden, Finland, Germany and the United Kingdom. Two samples (A and B) were prepared from known standards, whilst the third (C) sample consisted of the ultrapure

water used for the dilutions. Laboratories were required to analyse the samples on two different days with different calibrations. The results were processed according to the ISO 5725-2 standard.

The concentrations found in the test samples were also at levels comparable to many of the samples analysed for this project.

2.16.a Interlaboratory Test Results

Seven of the twelve laboratories responded to the interlab test. The results for the blank sample C, were not reported in this case. However, there was general agreement between the laboratories that for the blank sample, fluoride was less than 0.2 ppb, chloride less than 0.5 ppb and sulphate less than 0.5 ppb. For the BAS laboratory (**no. 7**) laboratory fluoride was undetectable, chloride gave a mean of 0.5 ppb and sulphate a mean of 0.8 ppb. Detailed results of samples A and B are shown below in tables 2.13 and 2.14, and summarised in table 2.16.

Table 2.13: Results of Sample A Analysis

Sample A Lab. No.	Fluoride ppb			Chloride ppb			Sulphate ppb		
	Day 1	Day 2	Mean	Day 1	Day 2	Mean	Day 1	Day 2	Mean
1	14.0	15.5	14.75	17.2	16.8	17.00	20.4	20.2	20.30
2				15.7	15.4	15.55	20.1	19.7	19.90
3	15.8	15.1	15.45	*12.6	*15.8	*14.20	20.4	19.4	19.90
4	18.0	17.9	17.95	16.6	16.2	16.40	20.4	20.2	20.30
5	18.5	18.9	18.70	16.8	16.6	16.70	19.9	20.2	20.05
6	16.5	17.1	16.80	18.1	17.2	17.65	20.4	20.7	20.55
7 - BAS	17.4	17.1	17.24	16.3	15.8	16.04	21.0	20.3	20.64
True concentration		16.0				16.0			20.0
Average		16.82				16.56			20.17
Std. dev. between labs		1.36				0.67			0.28

Table 2.14: Results of Sample B Analysis

Sample B Lab. No.	Fluoride ppb			Chloride ppb			Sulphate ppb		
	Day 1	Day 2	Mean	Day 1	Day 2	Mean	Day 1	Day 2	Mean
1	5.4	5.7	5.55	6.6	6.5	6.55	9.4	9.2	9.3
2				5.9	5.7	5.80	9.4	9.5	9.45
3	6.65	5.99	6.32	*11.4	*14.5	*12.95	10.2	10.8	10.50
4	8.3	8.7	8.50	6.6	6.6	6.60	9.0	8.9	8.95
5	7.7	8.0	7.85	7.2	6.6	6.90	8.8	9.2	9.00
6	7.6	6.9	7.25	6.9	6.2	6.55	9.7	9.4	9.55
7 - BAS	6.9	6.6	6.72	6.8	6.0	6.40	9.8	9.0	9.37
True concentration		7.0				6.0			8.0
Average		7.03				6.47			9.45
Std. dev. between labs		0.97				0.33			0.51

* Chloride values from laboratory 3 were discarded as outliers, with respect to variance at the 99.9% confidence level.

The laboratories were also asked to report their calibration ranges for the analytes. This information is summarised in table 2.15, together with the concentrated volume and column system used.

Table 2.15: Calibration Ranges for the Analytes

Lab. No.	Conc. Vol. ml	Calibration Range (ml)			Column System
		Fluoride	Chloride	Sulphate	
1	10	2-10	2-10	2-10	TAC2/AG12A/AS12A
2	9		0-2	0-10	TAC2/AG4A/AS4A
3	5	0-10	0-15	0-20	TAC2/AG4A/AS4A
4	10	1-25	1-25	1-25	AC10/AG10A/AS10A
5	2.5	0-20	0-60	0-60	AG11A/AS11A
6	20	0-2	0-5	0-10	AC10/AG10A/AS10A
7 - BAS	2	0-30	0-30	0-30	AG11A/AS11A

Table 2.16: Summary Results of Interlaboratory Tests

Analyte		True Concentration ppb	Grand Mean ppb	Std. Dev. ppb	BAS values ppb
Fluoride	A	16.0	16.8	1.36	17.2
	B	7.0	7.0	0.97	6.7
Chloride	A	16.0	16.6	0.67	16.0
	B	6.0	6.5	0.33	6.4
Sulphate	A	20.0	20.2	0.28	20.6
	B	8.0	9.5	0.51	9.4

The grand means agree well with the true concentrations, with one exception. The deviation for the low sulphate concentration is larger than expected; it is suspected that the true value is actually incorrect. This can be seen graphically, (figure 2.15) with the

clustering of the results well above the true value. The BAS values for all three species can be seen to be within the confines of the other laboratories which took part in this comparison. The BAS values for fluoride and chloride do not deviate greatly from the true concentrations depicted in figures 2.15, and for chloride, BAS performs better than the other labs.

2.17 Conclusion

This chapter has described, in detail, the samples studied for this thesis and the analytical techniques used throughout. These methods have been shown to be capable of accurately measuring, at the low levels required, concentrations found in the aerosol and snow samples.

Figure 2.1: The relative positions of Halley 4 and Halley 5.

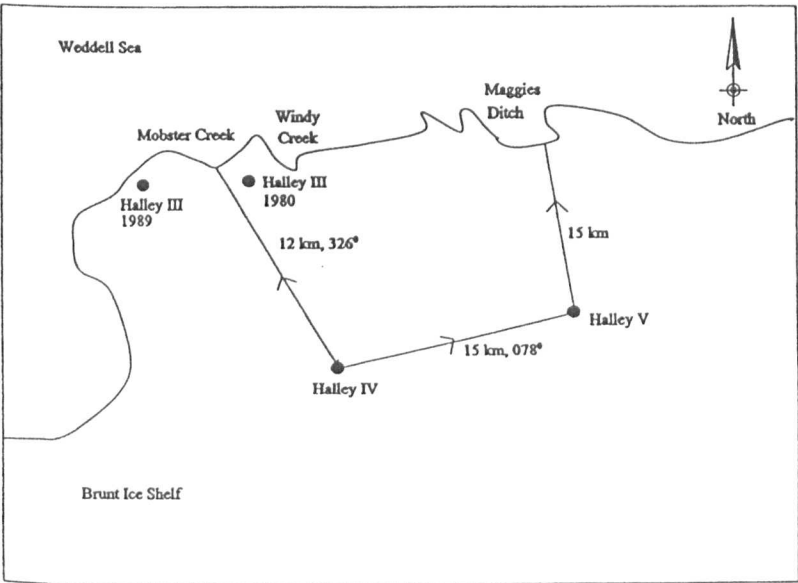


Figure 2.2: The sampling sites at Halley 4 and 5.

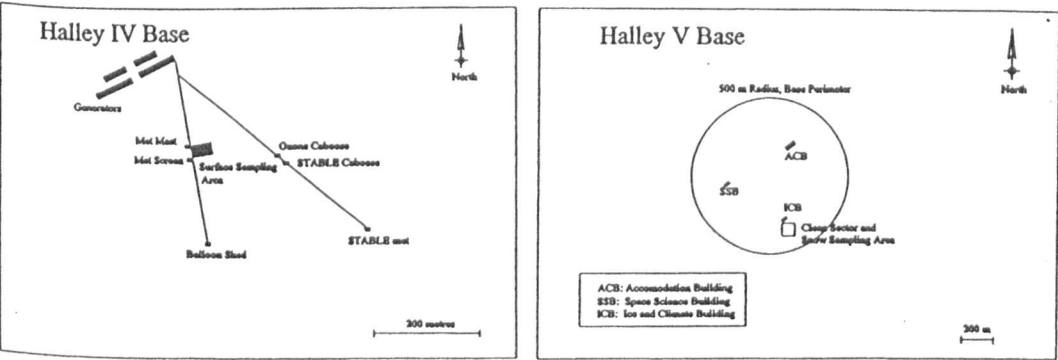


Figure 2.3: Filter sampling set-up at Halley.

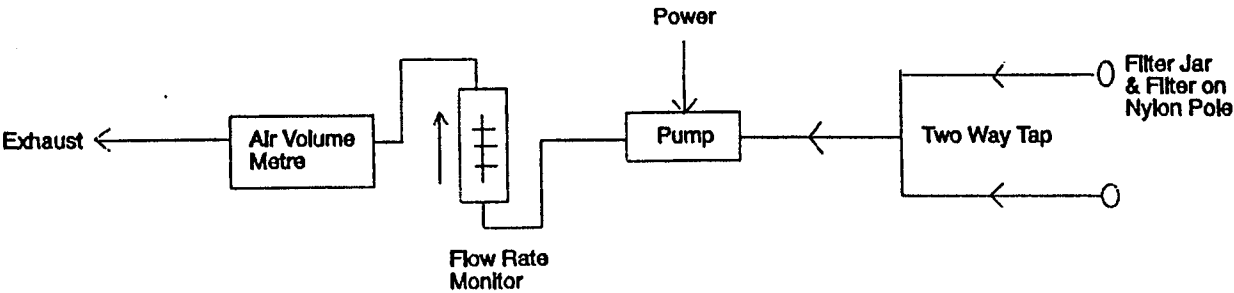
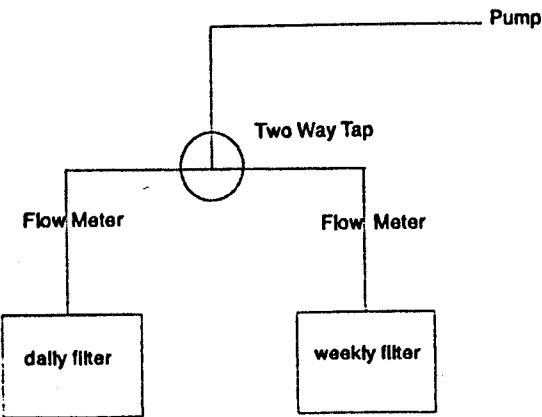


Figure 2.4: Simulated two-way valve set-up.
a: Intended filter/two way valve sampling set-up



b: Actual valve set-up

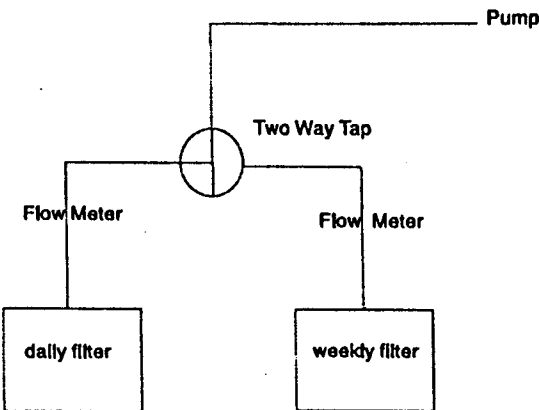


Figure 2.5: Graphical representation of the efficiency of extraction of particles from filters, for the major ionic species.

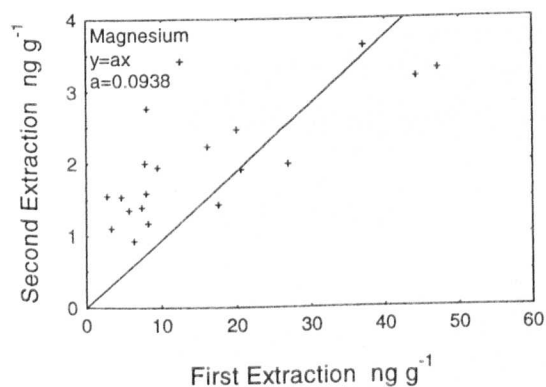
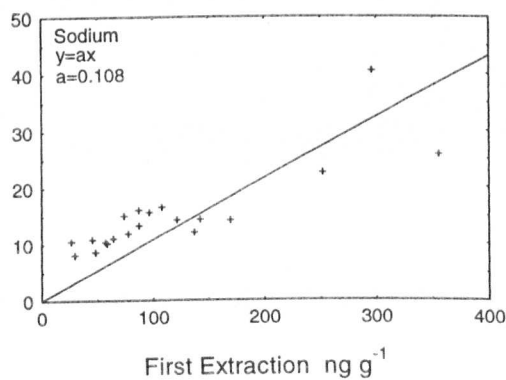
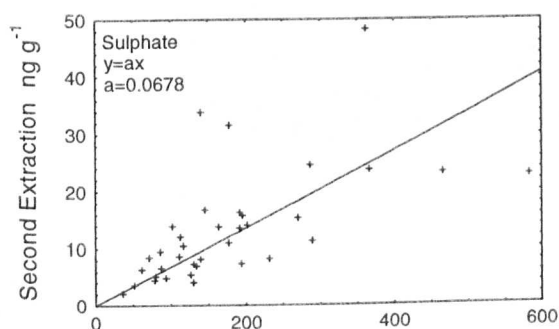
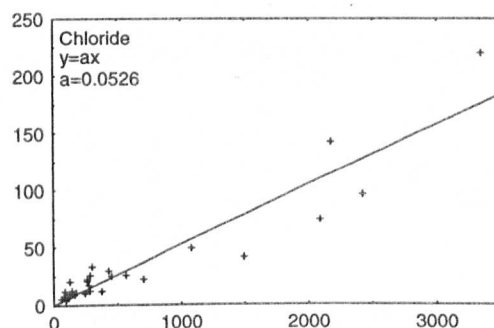
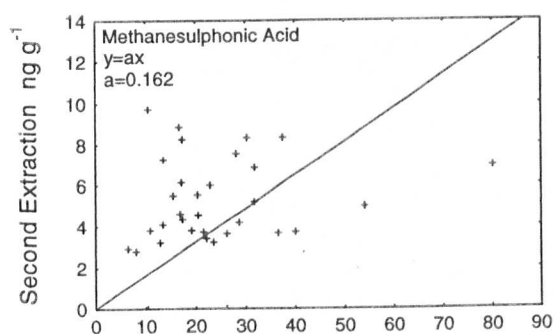


Figure 2.6: Surface snow sampler

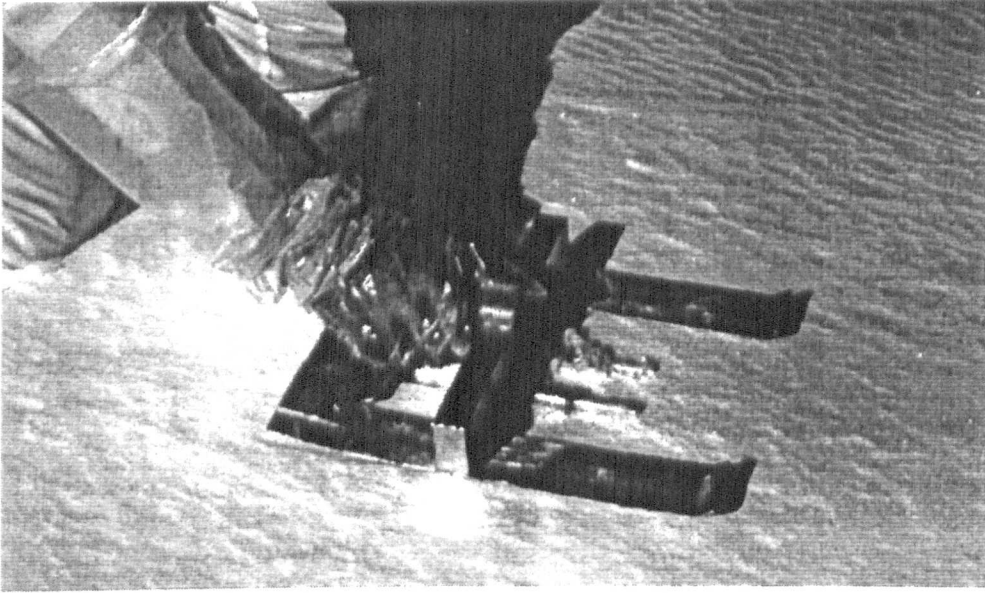


Figure 2.7: Accumulated snow sampler

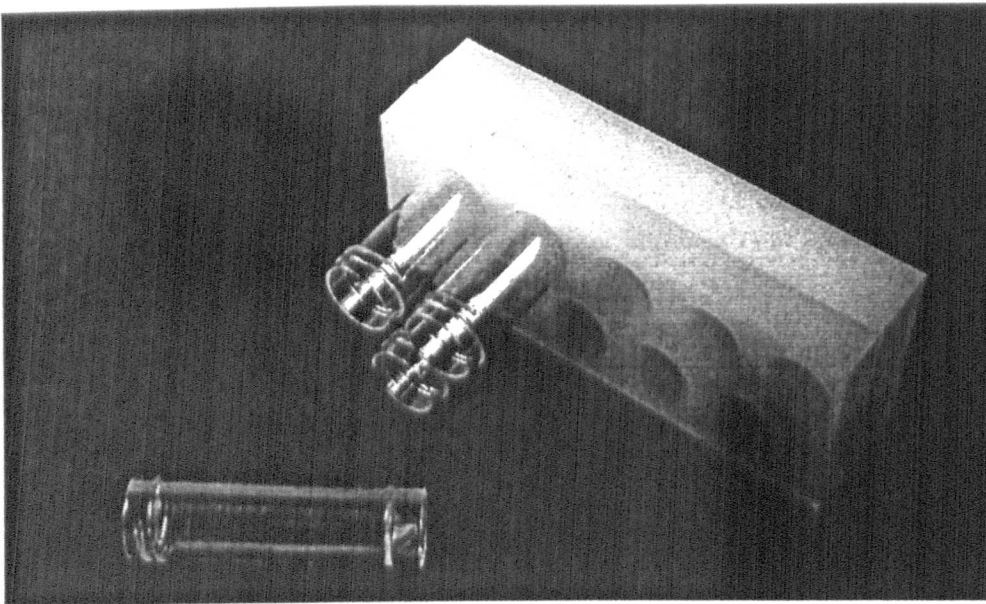


Figure 2.8: Position of samples collected on sastrugi

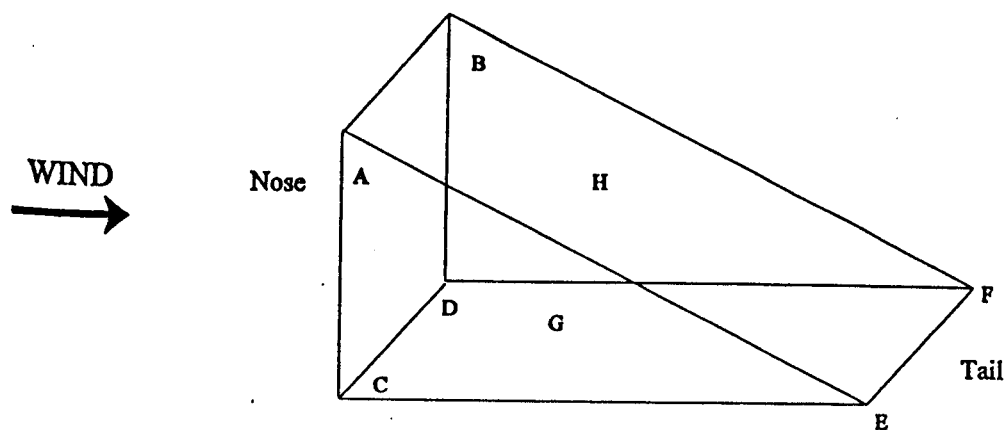


Figure 2.9: Example chromatogram using Method 3.

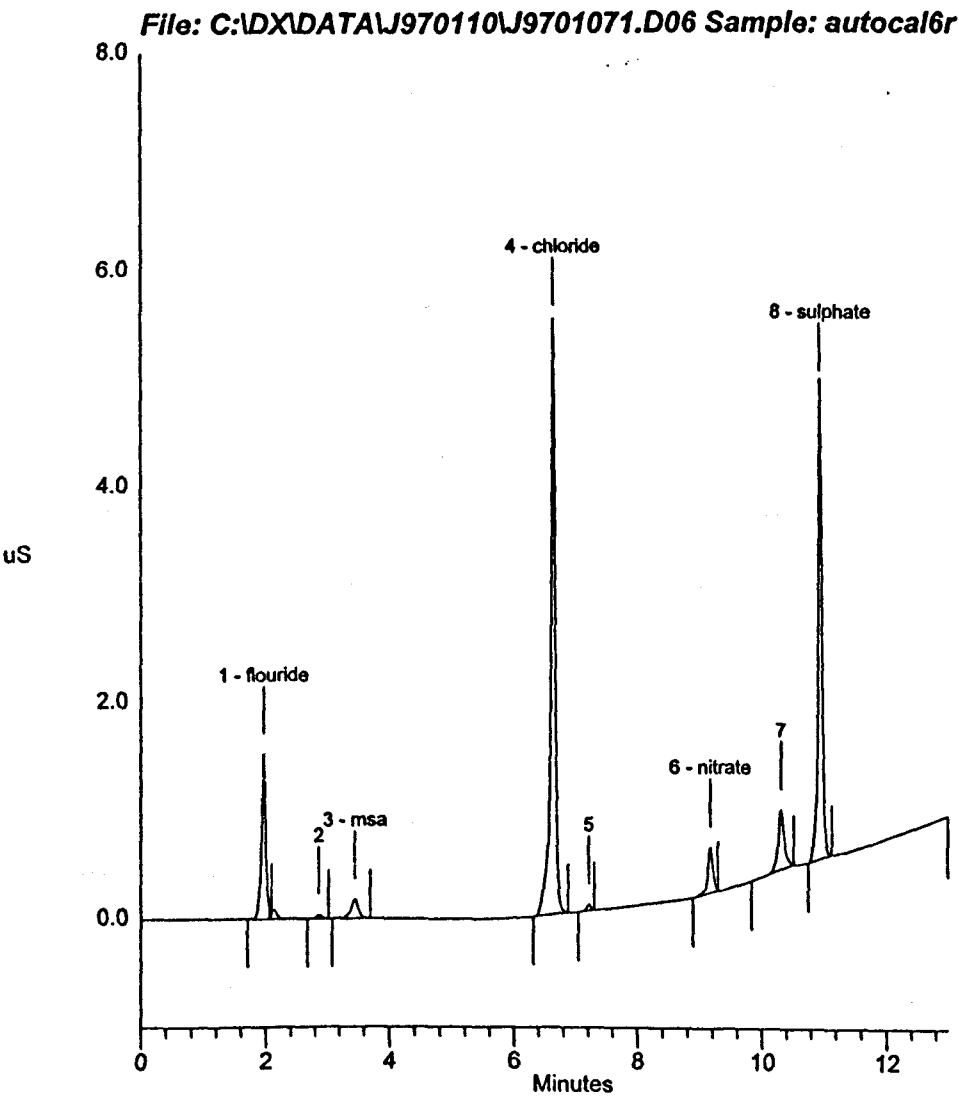


Figure 2.10: Example chromatogram using Method 4.

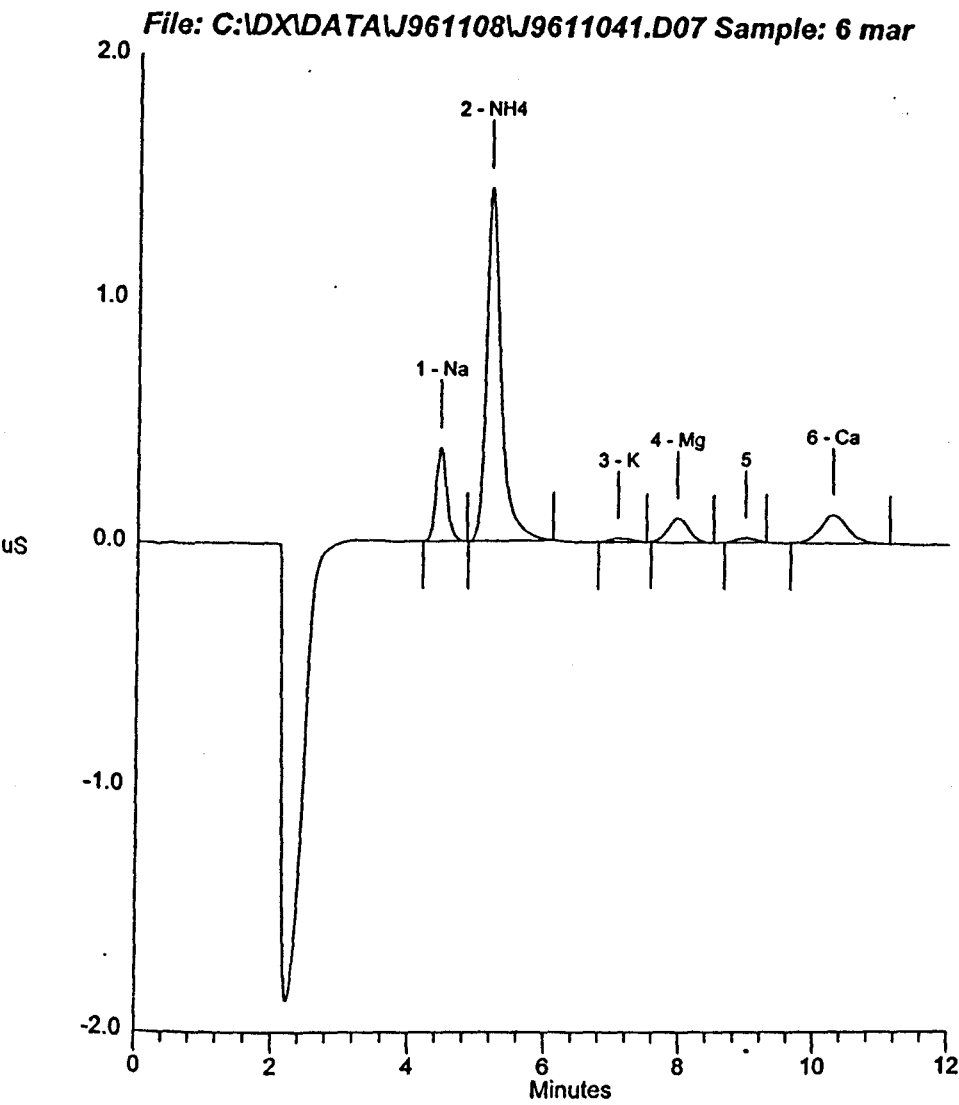
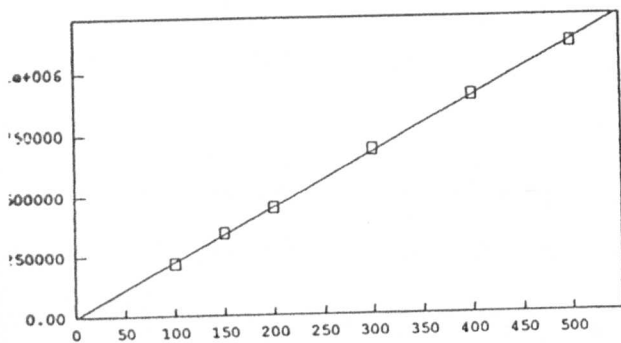


Figure 2.11: Ion chromatography calibration plots for MSA^- , Cl^- , Br^- , NO_3^- and SO_4^{2-} .

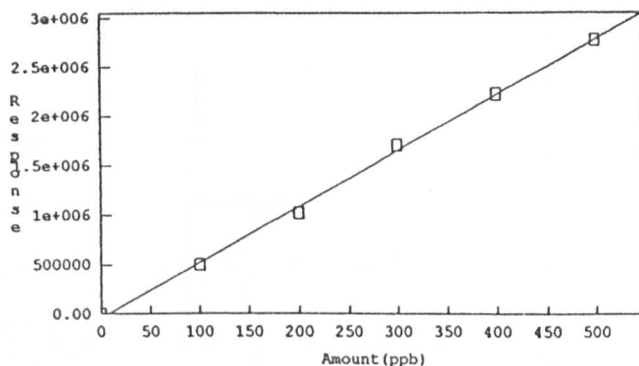
Method: C:\DX\METHOD\J9606128.MET

Component: msa
Fit Type: Linear
 r^2 : 0.999575
Amt = Resp * 0.0004453 + 0.2969
Resp = Amt * 2246 + -666.9
Standardization: External
Calibration: Height



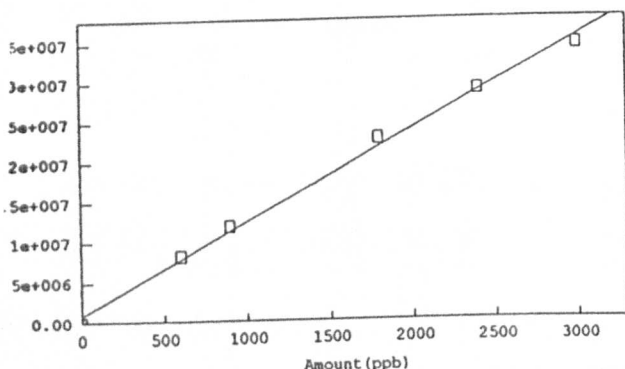
Method: C:\DX\METHOD\J9606128.MET

Component: nitrate
Fit Type: Linear
 r^2 : 0.998482
Amt = Resp * 0.0001775 + 6.674
Resp = Amt * 5632 + -3.759e+004
Standardization: External
Calibration: Height



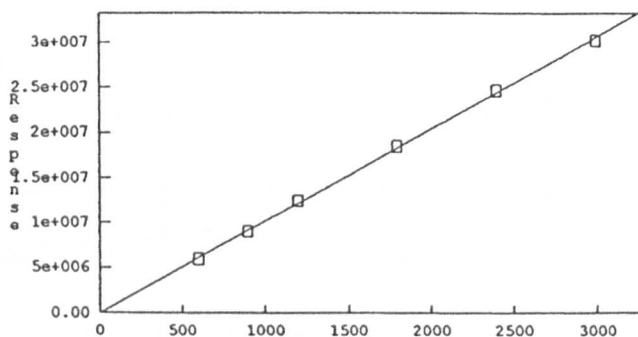
Method: C:\DX\METHOD\J9606128.MET

Component: chloride
Fit Type: Linear
 r^2 : 0.995898
Amt = Resp * 8.682e-005 + -82.73
Resp = Amt * 1.152e+004 + 9.529e+005
Standardization: External
Calibration: Height



Method: C:\DX\METHOD\J9606128.MET

Component: sulphate
Fit Type: Linear
 r^2 : 0.999235
Amt = Resp * 9.824e-005 + 2.048
Resp = Amt * 1.018e+004 + -2.084e+004
Standardization: External
Calibration: Height



Method: C:\DX\METHOD\J9606128.MET

Component: bromide
Fit Type: Linear
 r^2 : 0.999223
Amt = Resp * 0.001319 + 48.2
Resp = Amt * 758.2 + -3.654e+004
Standardization: External
Calibration: Height

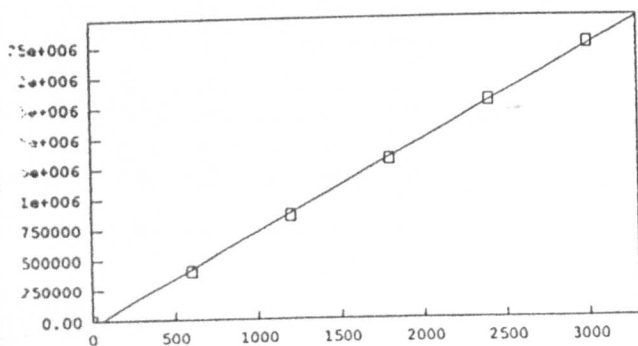


Figure 2.12: Ion chromatography calibration plots for Na⁺, K⁺, Mg²⁺ and Ca²⁺.

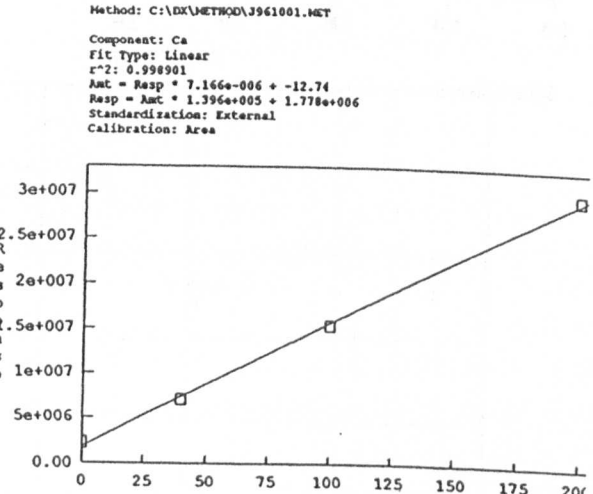
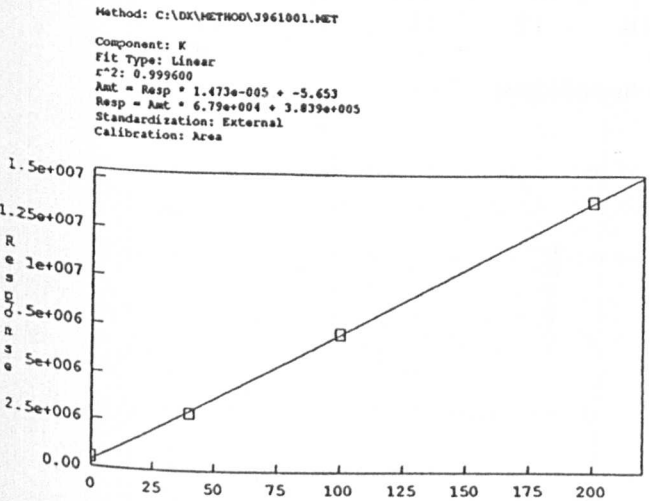
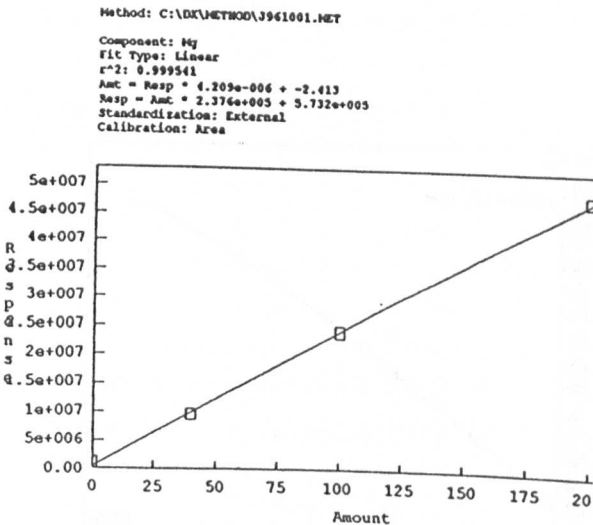
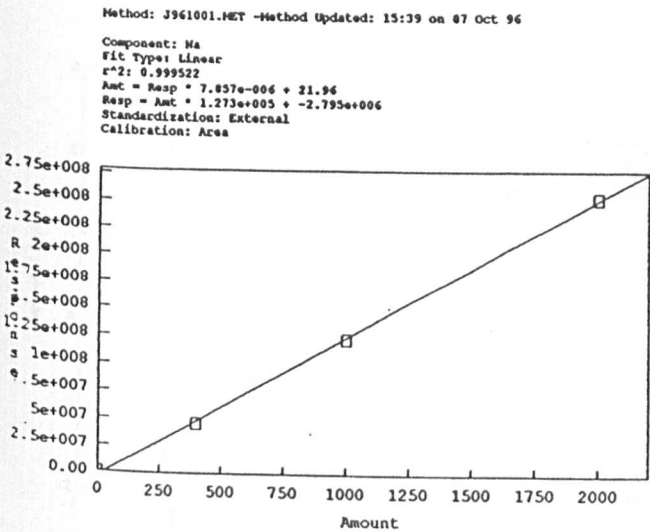


Figure 2.13: Atomic absorption spectrophotometry calibration plots for Na^+ and Mg^{2+} .

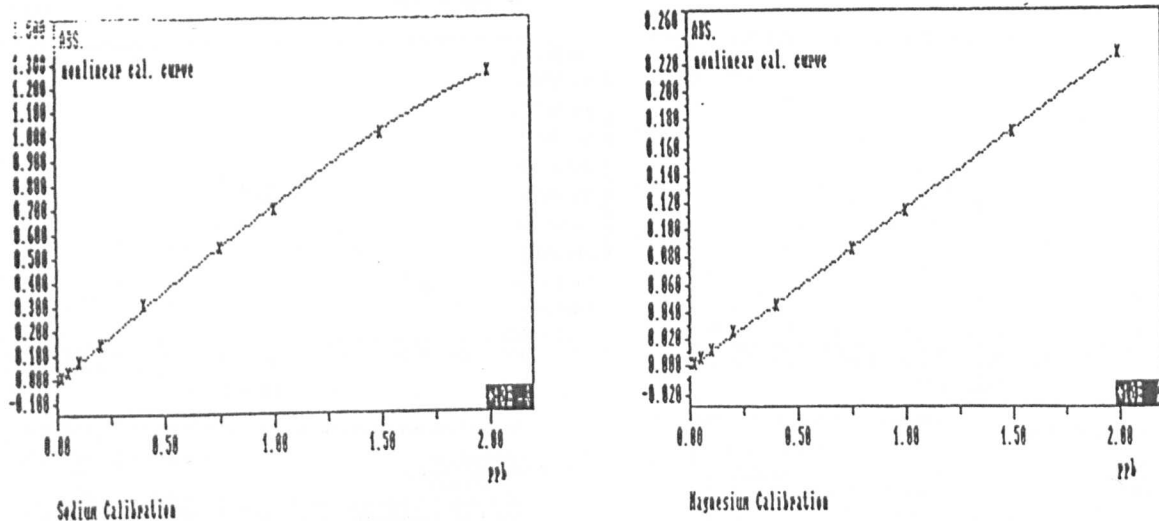


Figure 2.14: Flame emission spectrophotometry calibration plot for K^+ .

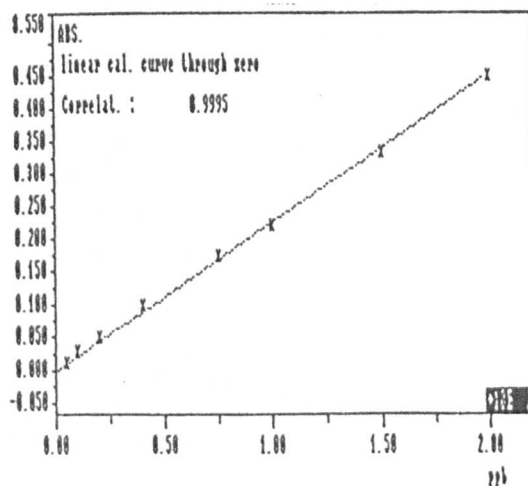
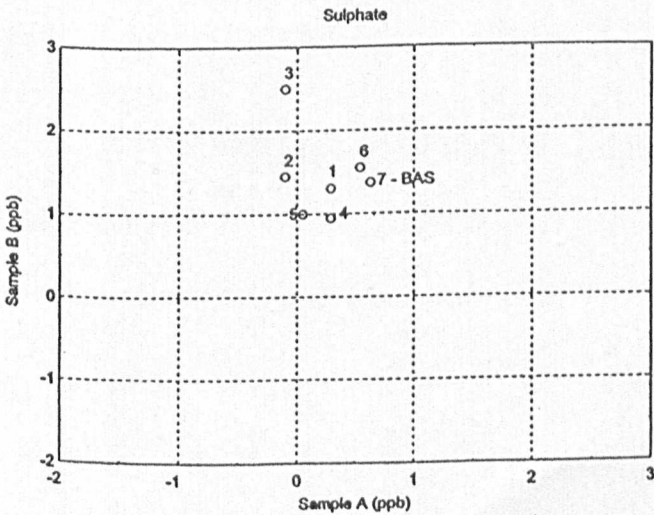
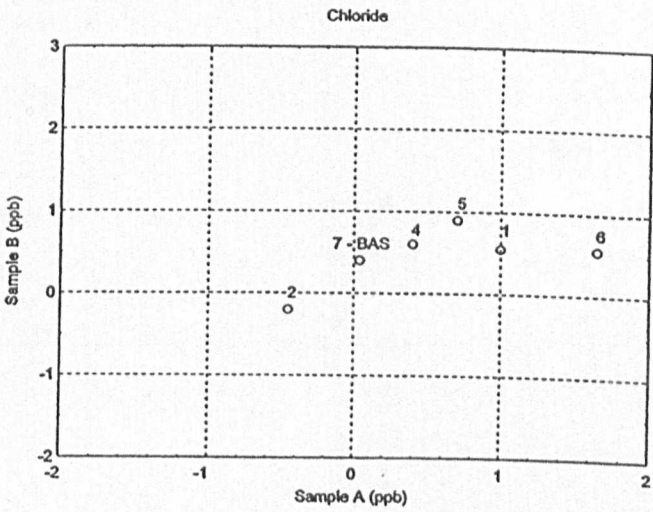
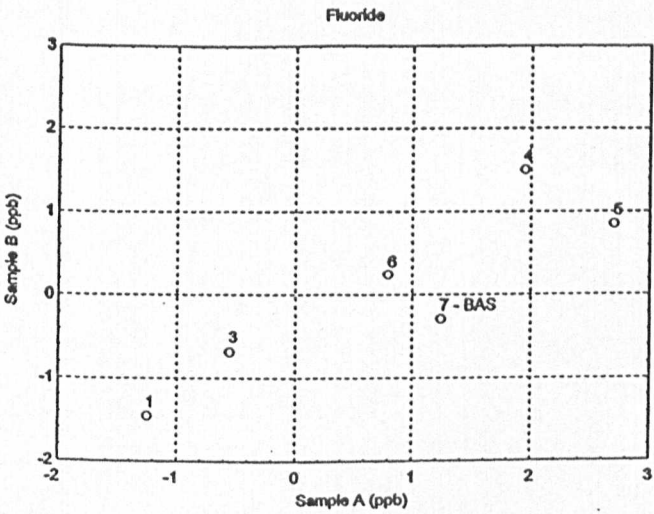


Figure 2.15: Observed deviations from the true concentration in this inter-laboratory comparison study



Chapter 3

Aerosol Chemistry in Coastal Antarctica

3.1 Introduction

The study of aerosol chemistry in polar regions is essential if we are to confidently interpret information obtained from ice cores. If the chemistry of present day Antarctic air is not better understood then we can never accurately use ice core chemistry to give us information on past climates.

This chapter aims to increase our knowledge of Antarctic aerosol chemistry. The seasonality of the aerosol species studied for this project, chloride, methanesulphonic acid, sulphate, sodium, magnesium, potassium and calcium, will be shown here. The data will be compared with other coastal Antarctic stations. Specific events in the data set will be examined and the local meteorology will be used to explain certain observations.

The aerosol records shown here are obtained using mixed cellulose ester filters, collected on a daily basis from Halley research station. Further information on sampling specifics can be found in chapter 2.

3.2 Sea Salt Species

Sea salt is by far the largest component of coastal Antarctic, primary aerosol particles. Its major ions are chloride, sodium, magnesium, sulphate, calcium, and potassium, these being the sea salt species which this study concentrates on. Bromide, boron, strontium and fluoride are also present, but in smaller amounts and were not measured for this project. The concentrations of the comprising ions in sea water are shown in table 3.1.

Table 3.1: The concentration of the major ions in sea water (g kg⁻¹ sea water), normalised to 35 ‰ salinity .

Ion	Average Value	Ion	Average Value
Chloride	19.353	Potassium	0.399
Sodium	10.775	Bromide	0.0673
Magnesium	1.2945	Boron	0.0046
Sulphate	2.712	Strontium	0.0080
Calcium	0.4121	Fluoride	0.0013

NB: Taken from Handbook of Marine Science, [1974].

3.2.a Sea Salt Aerosol Sources

Sea salt particles are produced by mechanical disruptions at the ocean surface. This mainly occurs by bubble bursting, resulting from entrainment of air, induced by wind stresses [O'Dowd et al., 1997]. Bubbles reaching the surface of the ocean begin to protrude beyond, allowing the liquid to drain from the upper protruding surface and creating an unstable medium, which subsequently collapses into fragments. When the upper film

breaks an excess hydrostatic pressure is left behind, which causes a jet to form and ejection from the lower half of the original bubble. This jet then breaks into drops [Twomey, 1977]. Two separate types of drop are formed by this means. Fragmentation of the bubble cap results in film droplets, whereas breakup of the water-jet, formed by the collapse of the bubble cavity, produces jet drops [Wu, 1993].

In addition to bubble bursting, the tearing of wave crests by winds, creates spume droplets [Wu, 1993]. In this chapter I will also hypothesise an additional source of sea salt particles, other than the expanses of open water traditionally thought to be necessary in order to create sea salt particles [Hall & Wolff, in press]. This source takes the form of a concentrated surface layer of brine, sitting on top of newly formed winter sea ice. Frost flowers, which form above the vapour phase of this slush layer, are thought also to aid incorporation of sea salt particles into the atmosphere. This discussion is continued in section 3.4, later in this chapter.

3.2.b Sea Salt Size Distribution

Sea salt particles have three mode size distributions, depending on the way they are formed. Jet drops tend to have radii between $r \approx 1\text{--}2\ \mu\text{m}$, with approximately 4-6 jet drops produced per burst bubble. Film drops are far more numerous, with around a 100 drops per bubble, but are much smaller than jet drops, with $r \approx 0.1\text{--}0.2\ \mu\text{m}$. Spume drops produce the 'giant' sea salt particles, with r greater than $\approx 100\ \mu\text{m}$ [O'Dowd et al., 1997; Twomey, 1977].

Blanchard [1967] estimated that on average 10^{18} - 10^{20} bubbles burst at the ocean surface per second. This corresponds to 10^3 - 10^4 megatons per year [Woodcock, 1953], which is easily comparable to industrial emissions. This being the case, it is vital to understand what role sea salt plays in Antarctic aerosol chemistry.

3.2.c The Significance of Sea Salt

Having established that sea salt is by far the largest component at coastal Antarctic sites [Wagenbach et al., in press, section 3.2], such as Halley research station, we should attempt to identify why sea salt is important. The number concentration and composition of aerosols in general can affect the Earth's climatic system. Aerosols can alter the global energy budget, both directly and through their influence on the formation of clouds, by affecting the absorption or scattering of solar radiation [Hansen and Lacis, 1990]. Sea salt is also important in palaeoclimatic studies. Authors have suggested that its concentration can be used to infer aspects of the past marine environment. Generally, such studies have assumed that sea salt concentrations are related to a combination of sea ice extent and wind speed. It has been suggested that sea salt concentrations can be linked to changes in atmospheric circulation patterns and regional sea ice extent [Peel and Mulvaney, 1992]. Cores drilled at Dome C, in Eastern Antarctica, have shown that during glacial times the concentration of sea salt was five times higher than levels found today. This has been used to imply that stronger atmospheric circulation once existed, associated with an increase in storminess which compensated for the larger sea ice extent at these times [Petit et al., 1981]. However, little work has been carried out to assess what influences sea salt

concentrations in either coastal or central Antarctica in the present day.

Aerosol sea salt particles are also important because they have the potential to take part in a series of heterogeneous air reactions in the remote marine boundary layer. These result in the release of large fluxes of reactive halogens, such as HCl and HBr [Mozurkewich, 1995; McInnes et al., 1994]. Other reactions involving chloride and bromide can subsequently affect the concentration of ozone, hydrocarbons and cloud condensation nuclei (CCN) [Vogt et al, 1996].

Traditionally, cloud condensation nuclei (CCN), (particles that act as a centre for growth for condensation of water to droplets), have been thought to consist mainly of non sea salt sulphate particles [Charlson et al., 1987]. It is now thought that sea salt particles with radii $> 0.5 \mu\text{m}$ could also provide a strong CCN source. Sea salt would therefore be involved in a climate feedback mechanism [Latham and Smith, 1990]. Sea salt can be preferentially activated in CCN, over nss-sulphate, due to a lower activation threshold compared to similar sized sulphate particles [O'Dowd et al., 1997]. Therefore, predicted climate changes based solely upon changes in nss-sulphate CCN concentrations are likely to be substantially overstated, if sea salt is not taken into account. Indeed, present models fail to predict the increase in sea salt concentrations found in snow during an ice age [Genthon, 1992], and do not stand a chance of doing so accurately if the sources are misunderstood. Later in this chapter we will see that using open water, as a source to model sea salt, may also be incorrect (see section 3.4).

3.2.d Determination of Aerosol Sea Salt Concentrations

For this project, sea salt aerosol concentrations are calculated from the sodium concentration, assuming all sodium observed originates from sea salt production. Sea salt is calculated as:

$$35/10.775 * [\text{Na}^+] \text{ [Walton et al., 1974].}$$

Sodium is the typically used reference element for sea salt determinations and is regarded as a conservative species. Chloride could also be used, but this can have several drawbacks. There is a possibility that chloride causes sea salt concentrations to be underestimated, due to mobilisation of the chloride component from airborne sea salt particles, or from sea salt already accumulated on the sampling medium [Wagenbach et al., in press; Cunningham & Zoller, 1991]. Chloride can also exist in excess, by the formation of HCl in the atmosphere, due to the reaction of H_2SO_4 with sea salt particles [Legrand & Delmas, 1984; Delmas et al., 1982]. Besides sea water, chloride also has volcanism as a natural source [Clausen & Langway, 1989]. However, there can also be a depletion of sodium, due to precipitation of Na_2SO_4 , and this will be discussed later in this chapter and also by Wagenbach et al., [in press]. This could cause a slight underestimation of sea salt concentrations. However, in general, sodium is the preferable choice for sea salt determinations in a marine environment.

3.3 Seasonality of Aerosol Sea Salt at Halley

Figure 3.1 shows the daily, raw data for sea salt components measured at Halley. Figure

3.2 is the same data, but displayed as monthly averages. The final sea salt values, calculated as previously described, using sodium data are shown as daily, raw values in figure 3.3a and monthly averages in 3.3b.

The annual mean aerosol sea salt concentration at Halley is 162 ng m^{-3} . This value is relatively low in comparison with reported findings at other coastal sites. Neumayer station, situated closest to Halley, has an annual mean of 850 ng m^{-3} [Wagenbach et al., in press]. The value for Mawson, on the eastern coast of Antarctica, is 330 ng m^{-3} [Savoie et al., 1993] and for Dumont D'Urville, on the Terre Adélie coast, 1400 ng m^{-3} [Wagenbach et al., in press]. On the peninsula, Palmer station gives a value of 3900 ng m^{-3} [Savoie et al., 1993] and Marsh station, on the very northern tip of the peninsula, gives 10200 ng m^{-3} [Savoie et al., 1993]. The only data currently available for central Antarctica are from South Pole, which has an annual mean of 61 ng m^{-3} [Tuncel et al., 1989]. Figure 3.4 shows the position of these bases in relation to Halley.

There are a number of reasons for differences between these coastal stations. Sampling campaigns are often carried out under very different conditions. Filter sampling media, cleaning protocols, collection, extraction and analytical techniques vary widely from site to site and are not always reported in the literature in great detail. The location of the sampling site and local meteorology can also affect the concentrations, particularly if sampling is near open water, or strong katabatic circulation patterns. Until a standard sampling protocol is established the former will continue to be a problem and this should always be considered when comparing data.

The fact that the aerosol sampling at Halley, takes place at no more than 2 metres above the surface may be partly responsible for the low annual mean obtained here. It is possible that sideward drift of snow cleanses the air at times, before it is actually sampled on the filter faces. This may explain the much higher value at Neumayer, the station closest to Halley base, where the filter intake tube is approximately 7 metres above the surface [Wolff et al., in press]. At this level the influence of drifting snow may be less important. Presumably at greater elevations the air would rarely come into contact with drifting snow and would not be filtered, or cleansed to the same degree.

At both these stations it is also possible that size selection occurs during sampling [Wagenbach et al., in press], either due to non-isokinetic flow at the air intake tube, or due to the effect of gravity on heavier particles. At Halley the filter face is located inside a downward pointing cylinder, acting as a protective wind/snow shield. This results in the air velocity inside the cylinder being greater than that outside. Exclusion of some larger sea salt particles may therefore occur, compared to the actual aerosols in the main air stream [Murphy, 1984]. Figure 3.5 diagrammatically represents particle behaviour at sampling inlets under non-isokinetic conditions. The diagram shows the particle trajectory when the inlet air velocity is greater than the main air stream velocity.

From Murphy, [1984], it can be calculated that particles greater than $20\text{ }\mu\text{m}$ are not collected. In some cases the downward pull of gravity for larger sea salt particles will be greater than the sampling velocity of the pump, again it can be calculated that this will affect particles greater than $20\text{ }\mu\text{m}$. However, studies on the size of sea salt particles have

indicated that close to their source they do not exceed $10\ \mu\text{m}$, and that further inland they continue to decrease in size [O'Dowd, 1997]. The effect of size selection may therefore be minimal at Halley, although it is possible that some underestimation of larger particles occurs.

The lower annual mean at Halley may also be due to its more southerly position. It has the shortest open water season, compared with all the above coastal bases and even during summer there are no vast areas of open water. Therefore, the amount of open sea available to produce sea salt aerosol in the traditional way, by mechanical mobilisation, such as bubble bursting from sea spray, is limited (see section 3.4).

It is likely that the most influential reason for the lower level is the predominant easterly wind direction at Halley, from the interior, and not from over the sea. Approximately 40% of the winds occur from the east and $\approx 15\%$ from east north east [Hanssen-Bauer, 1992]. At Neumayer, where sea salt concentrations are considerably higher than Halley, the predominant easterly winds pass directly over open water only 6.5 km away, before reaching the station [Wolff et al., in press]. The nearest open water to the east of Halley, is the Ross Sea, on the opposite side of the Antarctic continent. There is therefore no readily available source of sea salt particles east of Halley. Even in the less common westerly - west south west direction (where winds occur between 4-13% of the time depending on the season [Hanssen-Bauer, 1992]), Halley is some 15 km from the ice shelf edge. For more detailed information on the climatology of Halley refer to chapter 1 of this project, also König-Langlo et al., [in press] and Hanssen-Bauer, [1992].

Maximum sea salt concentrations at Halley are found during the winter months May-September (mean 206 ng m^{-3}) and are shown in figure 3.3a and b. This peak during the winter is also observed in aerosol records from Mawson [Prospero et al., 1991], Neumayer [Wagenbach et al., in press] and South Pole, where winter concentrations are an order of magnitude greater than summer values [Shaw, 1989; Bodhaine et al., 1986]. Maximum aerosol sea salt loadings at Dye 3 in Greenland [Mosher et al., 1993], also occur during winter. Several seasonally resolved firn cores also indicated a peak during the winter [Minikin et al., 1994; Mosley-Thompson et al., 1991; Mulvaney and Peel, 1988].

These high winter sea salt loadings presents us with a problem if we believe that sea salt only originates from open water, via long range transport. If this is the case we would assume that maximum salt production takes place during the summer, when there is most and nearest open water to create the sea salt aerosols. The fact that sea salt is actually peaking during the winter, when ice cover is at its most and open water at a minimum, indicates that there must be another 'unknown' source of sea salt production during this time, or that some other factor dominates.

This winter maximum has, in the past, been attributed to rapid, long range advection of sea salt particles from large, vigorously stirred, open water areas, followed by entrainment into down slope winds [Parish, 1988]. Due to the lack of a known local source, many authors have linked the source strength and transport to Antarctica of sea salt aerosols to an increase in storminess [Isaksson et al., 1996; Savoie et al., 1993; Peel & Mulvaney, 1992; Shaw, 1989; Mulvaney & Peel, 1988; Wagenbach et al., 1988; Legrand & Delmas, 1984;

Cunningham & Zoller, 1981], but as yet it has not been possible to test whether this hypothesis is true. This would place the winter sea salt source north of the ice edge, with a more effective long range transport pathway as the cause of the winter maximum. However, the higher winds necessary to aid this transport are clearly not seen. In fact there is only a slight tendency for higher mean wind speeds to occur at Halley during the winter [König-Langlo et al., in press], nor is there a marked change in wind direction. This discussion is continued in section 3.4, later in this chapter.

It is possible that long range transport could still occur, without the aid of strong winds. However, this seems unlikely in the case of sea salt, where rapid fall-off occurs in surface snow sea salt concentrations, by a factor 2 or more, with a distance of 100 kms inland from the ice shelf edge [Minikin et al., 1994; Mulvaney & Wolff, 1994; Gjessing, 1989; Legrand & Delmas, 1985]. This suggests that the main source of sea salt in coastal Antarctica is a local one, coming from relatively short distances.

Coastal polynyas, areas of open water created by strong winds and currents, could also be a contributing source. Winter shore leads develop amongst the sea ice, and together with polynyas, account for 5% of the total area of the Weddell Sea alone. An increase in spray and froth at the edge of these leads and ice floes, may then cause greater production of sea salt. This potentially influencing factor, as well as a link with storminess, is examined later in detail, by studying individual episodes of large sea salt input to Halley, in an attempt to establish whether a local meteorological event is linked to particularly high sea salt events (see section 3.4).

3.3.a Other Reported Aerosol Sea Salt Records

The Dumont D'Urville sea salt record is unlike the previously mentioned stations. Here, aerosol sea salt strongly peaks during the summer [Ducroz, 1996]. This is because the station is located on a small island, less than 1 km across, continually washed with sea salt spray. It is also quite far north, with latitude 66° . As a result the station experiences a much longer open water season than Halley and a smaller sea ice maximum, creating an environment of continuous sea spray over the island.

Marsh and Palmer aerosol sea salt records, both located on the Antarctic Peninsula, show no significant seasonality, but this may be due to the limited data set available [Savoie et al., 1993].

3.4 Daily Variability in Aerosol Sea Salt

As can be seen from figure 3.3a, the aerosol sea salt record at Halley experiences a large amount of variability between some samples. Although stations such as Mawson, Neumayer and South Pole have not undertaken such a high resolution (daily collections) sampling campaign as Halley, these stations also report significant sample to sample variability. In the case of Halley, there is up to a factor 60 difference between adjacent days during the winter, when the highest individual peaks occur. High events are also found in the summer, but are less pronounced. In the past it has not been possible to study the reasons behind these individual events in detail, as daily aerosol sampling is required to

observe daily changes in the data. The daily Halley samples now provide this opportunity and can be compared with the detailed three hourly meteorological observations which were also recorded. Specific high sea salt events were examined in comparison to meteorological features, in an attempt to explain these huge daily changes in sea salt concentrations reported here.

Ten events of the highest daily variability were investigated; four in 1991 (Figure 3.6a) and six in 1992 (Figure 3.6b). The associated wind speeds and directions for the day of high sea salt are also shown on these plots.

As previously mentioned, in the past it has been assumed that strong wind speeds are responsible for the sudden and sporadic increases in sea salt concentrations, particularly during the winter. It has been speculated that high winds bring in sea salt particles from distant, open water. Of the ten events examined here, the wind speeds on the day of high sea salt loadings, are not considered strong/high. The majority of wind speeds are found to be less than 5.1 m s^{-1} and all are less than 7.7 m s^{-1} (Figures 3.6a & b). On the day before the event, the speeds tended to be higher in all but four cases, but again only one exceeds 10.2 m s^{-1} . It should be mentioned here that the filters were removed between midday and 16:00, this can account for a slight leading in sea salt concentration, with regard to wind direction change, in some cases, where the filter may actually have been removed at 16:00 rather than midday.

From this detailed study of wind speed and high sea salt concentration we can conclude that

high local wind speeds are not a factor in causing elevated concentrations of sea salt and it is actually moderate winds that seem to be associated with these events.

Wind direction was also examined on these days. In eight of the cases, the highest sea salt concentrations were also associated with a change in wind direction, either on the day of or the day before the high event. In each of these eight cases this was from an easterly, offshore, direction to a westerly inland wind, for often no more than a day, until returning to an easterly wind. From this I present the following suggestion as to the initial cause of the high sea salt episodes.

3.4.a Additional Source of Winter Aerosol Sea Salt

Stronger offshore easterly winds open up an area of local water in the normally dense sea ice to the west of the station. The wind then changes to westerly, from over the open water, and decreases in strength. This decrease in strength prevents the open water immediately closing up, due to contra-wind direction, but allows transport of local airborne sea salt from above the ocean, into inland. The wind direction then changes back to the east and from over the continent, or the open water closes up and the supply of sea salt is cut off.

However, I have already speculated that an area of open water alone, cannot account for all the winter sea salt, as minimum concentrations are found during the summer when there is most open water. Whilst local open water may still be important, there seems to be something special about conditions during the winter, and an additional winter source must

still be found. One significant difference between winter and summer is that when offshore winds open up a coastal lead, or local polynya, rapid, new sea ice production will occur. When open water is exposed to the colder temperatures found during the winter, ice growth will be considerably faster due to rapid heat conduction from the warmer newly opened water to the colder air. For instance, an average temperature of -20°C can produce a sea ice coverage that is 20 cm thick, in less than 2 days [Perovich & Richter-Menge, 1994].

As the open water begins to freeze, and a thin layer of new, fresh sea ice is formed, the top surface of ice becomes covered by a surface skim of highly concentrated slush. This observation is well documented in the literature, particularly in the journals and reports of early explorers and scientists working both in the Arctic and Antarctic [Drinkwater & Crocker, 1988]. This moist surface layer is formed as the ice freezes out of the open water, leaving behind more concentrated brine. It can also be attributed to an upward expulsion of brine through capillary action, from the top portion of sea ice during cooling [Perovich & Richter-Menge, 1994; Drinkwater & Crocker, 1988]. Martin and Barrie, [personal communication 1998] suggest that the reason brine appears on the ice surface is due to the transport of brine from warm to cold, by a thermomolecular pressure gradient.

Laboratory studies by Richardson, [1979] showed that the original sea water, which has a salinity of 35, increases in concentration to 122 at -8°C , as it is left behind as surface brine on the newly formed ice surface. As temperatures drop, this surface brine further concentrates to 212 at -20°C [Richardson, 1979]. If this surface brine, present on new ice, is scavenged by the atmosphere by mechanical mobilisation, it will present a highly

concentrated, local source of sea salt particles.

In addition to this source, incorporation into the atmosphere could be further aided by the presence of frost flowers. These small, saline ice crystals form on the surface of young ice, in clusters of thin platelets or needles, usually extending 10-30 mm in height [Martin *et al*, 1995]. Figures 3.7a and b show photographs of these structures.

These flowers have been seen to occur on young ice over large areas of the Arctic and Antarctic [Drinkwater and Crocker, 1988; Martin *et al.*, 1996]. In particular they have also been observed around Halley [Ladkin and Colwell, personal communication]. They are the result of ice growth from the vapour phase over surface brine and as a consequence also become highly concentrated, using capillary action to draw brine into their structure [Perovich and Richter-Menge, 1994]. The surface layer of brine, once at the surface, forms an irregularly distributed slush layer from which the frost flowers can grow, with patches of bare ice inbetween [Newyear, personal communication 1998]. The greater surface areas of these frost flowers and the fact that they extend further into the air, in comparison to the surface brine alone, would make it easier for concentrated sea salt particles to enter the atmosphere. The fact that these structures would also be very fragile, may explain why only moderate wind speeds tend to be associated with high sea salt events. Higher speeds would inevitably destroy the flowers. Both the surface skim of brine and the presence of frost flowers are linked with fresh, new ice only. In older ice it is likely that the brine layer is rapidly lost, either through erosion, or by a covering of snow.

3.5 Fractionation of Sea Salt

As described above, moderate wind speeds and wind direction change are thought to create ideal conditions for a local source of winter sea salt. In addition to this, evidence is available to link the presence of a surface skim of concentrated brine on top of new, freshly formed ice, to the high aerosol sea salt concentrations found during the winter at Halley. This is the occurrence of fractionation in the sea salt aerosol during the winter months.

Fractionation of sea salt occurs when a component, or components, of sea water splits away from the main body of that sea water, leaving behind a deficit of the splitting species. It is most easily recognised by obtaining negative non sea salt sulphate concentrations, when using the following calculation to determine these values:

$$[\text{nss SO}_4^{2-}] = [\text{SO}_4^{2-}]_{\text{total}} - k[x]$$

where x is the reference sea salt component, usually sodium (or chloride), and where k is the respective bulk sea water ratio (BSW), $[\text{SO}_4^{2-}]/[\text{Na}^+]$. Obtaining negative nss sulphate values by this means, implies that the actual $[\text{SO}_4^{2-}]/[\text{Na}^+]$ ratio in the samples was lower than the reference BSW value usually used.

Figure 3.8 clearly shows a deficit in the Halley winter aerosol record of nss sulphate, of as much as -100 ng m^{-3} in the worst case, when nss SO_4^{2-} is calculated as described above. In order to gauge how much depletion is actually occurring, simple linear regression is applied to the plot of nss SO_4^{2-} versus Na^+ in figure 3.8, to obtain a downward correction of the bulk sea water ratio, k . By adding the gradient of this slope to the conventional bulk sea water

value (k), a corrected mean bulk sea water ratio is found, k^* [Wagenbach *et al.*, in press; Minikin *et al.*, 1994]. The regression line shown in figure 3.8 is based on the winter values only and is -0.143. k^* becomes 0.107, using sodium as the reference component, compared to the bulk sea water ratio of 0.252. This corresponds to a sulphate depletion of nearly 60%. Similar k^* values have been found for winter aerosol and snow at Neumayer and Dumont D'Urville [Wagenbach *et al.*, in press]. At these stations a k^* value of 0.075 [Minikin *et al.*, submitted] is used, indicating that fractionation is more apparent here. However, unlike Halley, aerosol samples at Dumont D'Urville and Neumayer are collected weekly and often fortnightly [Wolff *et al.*, in press], allowing filter faces to be in contact with air for longer. This may allow additional fractionation to occur to the aerosols already sampled on the filters. It should also be noted that the standard error for the gradient is found to be ± 0.01 [calculated using a regression analysis programme on Lotus 123 vs 5], which could make k^* as small as 0.097.

Sea salt fractionation, implied through negative non sea salt sulphate concentrations, has also been observed in snow samples on the Antarctic Peninsula by Aristarain *et al.*, [1982] and in snow and shallow firn cores in east Antarctica by Legrand and Delmas, [1985]. Depletion was also recorded in Antarctic ice by Ivey *et al.*, [1986] at Law Dome also in east Antarctica and on the Peninsula by Mulvaney and Peel, [1988]. These deficits have since been linked to fractionation of the sea salt component [Gjessing, 1989]. Legrand and Delmas, [1988] suggested that in central Antarctica up to 50% of sea salt may actually be fractionated. Minikin *et al.*, [1994] and Wagenbach *et al.*, [1988] both found enormous nss sulphate depletion in airborne sea salt particles at Berkner Island on the Filchner-Ronne Ice

Shelf; up to a factor 5 difference between SO_4/Na experimental ratios and the actual bulk sea water ratio.

Wagenbach et al., [in press] have suggested that the sea salt fractionation takes the form of mirabilite, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, crystallising out of sea water at temperatures less than -8.2°C . This was also predicted from laboratory studies of the freezing of sea water by Richardson, [1976].

To firmly establish which of the sea salt species is fractionating out in the Halley coastal aerosol samples, weight ratios (R) have been determined from gradients of scatter plots for magnesium, potassium and calcium versus sodium, figure 3.9. Both the K/Na ($R=0.037$) and Ca/Na ($R=0.04$) ratios, compared with the BSW ratios of 0.037 and 0.038 respectively, show that K and Ca are not fractionating significantly from sea salt. The ratios for winter alone are similar to those found for the whole year. The contribution to total sea salt is relatively small for these species anyway, and we can assume that they have no part to play in the negative nss sulphate numbers. The Mg/Na ($R=0.134$) ratio is slightly higher than the BSW ratios of 0.12. However, this is to be expected if we assume that sodium is being depleted, along with sulphate, when mirabilite is crystallised out. We can conclude firmly that sodium is the cation depleted with sulphate.

With this in mind it may seem more prudent to use magnesium as the reference element for calculating sea salt and non sea salt concentrations, as it appears not to take part in any fractionation process. Indeed, magnesium has been used in the past to avoid negative nss

sulphate concentrations [Ivey et al., 1986]. It does have an additional dust component, but this is likely to be fairly minimal at coastal sites. The primary disadvantage with using magnesium is that it is not commonly measured in ice cores and as the underlying reason for doing aerosol measurements is to gain information that will better our understanding of ice core chemistry, it seems pointless to use an ion that is not universally recorded. An additional problem is that magnesium occurs in low concentrations, which are often close to the detection limit (about 3 ng m^{-3} at Halley). The average annual value for the Halley aerosol samples was less than 7 ng m^{-3} . A final disadvantage with using magnesium is that it may move in deep ice cores. This has been reported in cores from Dolleman Island, which showed sodium and magnesium in phase with each other in the upper firn layers, but at depths below 10 m, magnesium formed two peaks either side of a sodium minimum [Wolff, 1996].

3.5.a High Events of Airborne Sea Salt

Laboratory tests carried out by Wagenbach et al., [in press] have attempted to imitate conditions that bring about this sea salt fractionation. Sea salt particle production was mimicked by creation of spume, jet and film droplets and the formation and subsequent freezing of air bubbles. None of these scenarios were found to have the same degree of fractionation seen in actual samples. The only test which could re-created the correct amount of sodium sulphate deficit was that which depicted a surface slush of brine on top of new, freshly formed ice, with Na_2SO_4 precipitating out and sinking in the ice layer, leaving behind the brine deficit. It therefore seems likely that the surface layer of brine is

indeed the previously 'unknown' local source for the large winter sea salt maximum.

Although, as seen from figure 3.8, a general trend exists with winter aerosol sea salt samples at Halley being fractionated, it is necessary to see if the ten events of particularly high sea salt at Halley are themselves individually fractionated. If they are, then it implies that the sea salt source for our actual samples can be the same as the source mimicked in the laboratory.

Figure 3.10 shows the sulphate to sodium ratio on days of high aerosol sea salt, plotted with the bulk sea water ratio for sulphate to sodium. This figure shows that the majority of high sea salt events were associated with significant fractionation. The high ratio in the summer episode (November), is not surprising, as summer sulphate to sodium ratios are greatly enhanced due to an excess of nss sulphate from sulphur producing algae [Minikin *et al.*, submitted; Gjessing 1989; Parungo *et al.*, 1986]. The winter episode during April, which appears not to be fractionated, could be explained by the fact that the sea salt value, although increasing by a factor 30, is still low when compared with the other 7 fractionated events of sea salt. The biogenic input on this day is also minimal, shown by a low methanesulphonic acid concentration, and yet the total sulphate value still indicates that some 40 ng m^{-3} of sulphate is present. This concentration is within the range of winter background values, established for non-DMS non sea salt in coastal Antarctica, of between $17 - 50 \text{ ng m}^{-3}$ by Minikin *et al.*, [submitted.]. This winter background value is thought to be due to long range transport from terrestrial, volcanic and stratospheric sources. In the very high sea salt events this background is negligible, but in smaller events, such as this

one, it will raise the sulphate/sea salt ratio significantly. The remaining unfractionated winter event can not be explained in this way and is assumed to be an anomaly. However, the fact that the majority of these high events did show significantly lower sulphate to sodium ratios does add further weight to the theory that the winter source of sea salt is the concentrated, and fractionated, brine layer on the surface of fresh sea ice.

3.6 Aerosol Sea Salt and Temperature

The temperature record was also examined on the ten days of high sea salt concentrations. Figure 3.11 is representative of the 10 events and shows 2 high sea salt episodes in 1991 and 2 in 1992, plotted with the corresponding temperature for the time period. In all cases the temperature is well below -8.2°C , (the temperature necessary to freeze mirabilite and thus initiate fractionation). Other than the dependence on this temperature, there is no correlation between high aerosol sea salt events and the Halley daily temperature record.

3.7 Conclusions and Recommendations

The high resolution data available at Halley enable investigation of specific events, such as unusually high concentrations in comparison with daily meteorological records. The sea salt concentration at Halley peaks during the winter months, indicating an unknown source of winter sea salt aerosol. It has been suggested that this source is a thin layer of concentrated brine which sits on the surface of fresh, new ice, formed after an associated wind direction change. In addition to this, it is speculated that frost flowers play a

significant role in the incorporation of concentrated brine into the atmosphere. High wind speeds appear not to increase the likelihood of high episodes of sea salt and it is in fact the more moderate winds which can be linked to this. Back trajectory analyses would be useful here, and will be investigated later in section 3.11, as they could provide evidence of the longer range transport pathways of air masses. However, the rapid fall off in sea salt concentration with distance inland, indicates that the sea salt source is a local one.

Fractionation of the sea salt component, occurring during the winter, has been previously reported in the literature. The probable sea salt source for this fractionation has been identified as brine sitting on top of sea ice surfaces. The fact that high sea salt events, which dominate the total budget at this coastal site, were also found to be significantly fractionated supports this theory.

This project has shown that without a standard sampling protocol it can be very difficult to accurately compare aerosol records from different sites. At the very least all aspects of the collection method should be reported. Further investigation of the effects of drifting snow on aerosol concentrations is needed and will be discussed in later chapters. Clarification as to whether sampling height plays a part in altering concentrations is also required. It would also seem prudent to continue with daily sampling at other sites around the coast and particularly in central Antarctica, where aerosol records are relatively sparse. If, as found here, most high episodes of sea salt are associated with fractionation, then by mimicking the fractionation process in the laboratory, or even better proving it occurs in the field, we will be able to confirm the source of winter sea salt aerosol. Collection of the

surface brine and frost flowers on fresh, new sea ice is also needed to clarify the processes at work here.

In conclusion, there are two potential sources of sea salt to Antarctica aerosol and snow: firstly, 'normal' sea salt, un-fractionated, from areas of open water and secondly, 'fractionated' sea salt, probably from newly formed sea ice surfaces. The relative areas of the two sources need to be determined. Source one will dominate at lower latitudes and in air transported from longer range. However, the concentration of sea salt will be more, in the second.

The spatial extent of this second source, (and the fractionation process), needs to be established to enable accurate interpretation of ice core records. It is almost certain that fractionation dominates the sea salt component at coastal locations, with significantly negative nss sulphate values found in cores from the Filchner-Ronne Ice Shelf [Minikin et al., 1994], at Berkner Island [Wagenbach, 1994], at Dolleman Island and on the Palmer Land Plateau [Mulvaney and Peel, 1988]. The extent to which fractionation reaches into central Antarctica must also be further investigated. This is essential for the interpretation of ice cores and non sea salt sulphate concentrations from them, as any fractionation will affect the sea salt sulphate to sodium ratio used to calculate nss-sulphate values.

Altitude will also influence the effect of fractionation. This is seen in cores drilled at Dolleman Island and on the Dyer Plateau, both at similar latitudes, but differing altitudes (398m and 1943m respectively). In the top 50 m of core, 28% of the total number of

samples at Dolleman Island gave negative nss sulphate values, but in comparison only 0.6% were seen at the more elevated Dyer Plateau. Moving inland, the effect of fractionation also seems likely to be less. However, negative nss sulphate concentrations are still seen in an ice core from Siple station [Mosley-Thompson, 1991], and in a shallow firn core from Coats Land [Mulvaney, personal communication]. At very continental inland sites it is unlikely that substantial negative nss sulphate values would be obtained, (and fractionation observed even if actually occurring) as the concentrations of sodium (used to calculate nss sulphate), are very low. For instance, in ice cores from Dronning Maud Land, sodium rarely exceeded 30 ng g^{-1} [Isaksson et al., 1996]. These low concentrations are also observed at South Pole [Whitlow et al., 1992].

At coastal locations, and on the Antarctic Peninsula, fractionated sea salt does indeed dominate and is important over ice shelves. Further inland the evidence is less clear. It is possible that longer range transport, from lower latitudes with open areas of water, may contribute to inland records. But this still does not explain the extent of the winter maximum. While there could be a greater penetration of cyclonic systems into Antarctica in winter, the fact that sea salt still peaks during winter in these cores, could also imply that open water is not the determinant source. Fractionation could still be important here, just not seen so readily due to the lower sodium values. This requires further study.

The individual high concentration events, seen in the sea salt record, dominate the total budget at Halley. These fractionated episodes, produced from concentrated brine on the surface of sea ice, will be the values that eventually become incorporated into coastal ice.

Sea salt records from coastal cores may therefore actually be giving us information on the extent of new, fresh sea ice. If this is the case, our interpretation of sea salt ice core data may have been incorrect in the past. Ice cores may instead be used to infer the local temperature, sea ice extent and possible wind direction at the time of core formation.

3.8 Sulphur Species

For this study two biogenic sulphur species were examined, methanesulphonic acid (MSA or $\text{CH}_3\text{SO}_3\text{H}$) and non sea salt or excess sulphate (nss SO_4^{2-}). MSA can be measured directly using ion chromatography, but the latter species is determined from total sulphate concentrations, after a sea salt component is subtracted. This calculation will be expanded upon in section 3.8d.

3.8.a Particle Formation and Size Distribution

A major portion of trace impurities found in central Antarctic air [Shaw, 1979] and snow [Legrand and Delmas, 1984; Delmas et al., 1982] exists as secondary aerosol derived from the nucleation of atmospheric trace gases. Biogenic marine sulphur is a secondary aerosol, the product of gas to particle conversion processes [Shaw, 1989], with particles being formed in one of two ways. Firstly, completely new particles can form as gas molecules condense together, eventually forming an Aitken particle. These are the smallest particles of interest to us and probably range in size from about $4 \times 10^{-3} \mu\text{m}$ radius to an upper limit of about $0.1 \mu\text{m}$ radius [Brimblecombe, 1986]. Secondly, nucleation or coagulation on the

new particle (or other existing particles) can occur, either homogeneously or heterogeneously [O'Dowd et al., 1997]. Consequently, this can increase the size of existing aerosol particles, with non sea salt sulphate aerosols ranging in size from the smallest sub-micron Aitken particles, up to larger $1\text{ }\mu\text{m}$ aerosols. 85% of methanesulphonic acid and non sea salt sulphate particles studied in the Southern Drake Passage were found to be less than $0.25\text{ }\mu\text{m}$ in radius [Pszenny et al., 1989]. Saltzman et al., [1983] also found that MSA and non sea salt sulphate existed mainly in the sub-micron range. However, MSA can also be larger in size in comparison to nss SO_4^{2-} and can consequently lead to slightly longer lifetimes of nss sulphate with respect to MSA [Pszenny, 1992].

The residence time in the atmosphere for Aitken particles is only of the order a few days; coagulation reduces their number concentration and increases their average size, with time. However in general, sulphur aerosols have a longer lifetime of 30-95 days [Shaw, 1979], but lifetimes can be considerably enhanced for injections of volcanic sulphur into the stratosphere, where residence times for these sub-micron particles can be from one to a few years [Shaw, 1989].

3.8.b Sulphur Aerosol Sources

Apart from sea salt sulphate, the total sulphur budget comprises biogenic, marine sulphur, sporadic episodes of volcanic input, as well as a constant volcanic background level, continental crustal sulphur and an anthropogenic influence. The various components that make up the total sulphur budget are summarised in figure 3.12 and described in detail

below.

3.8.b(i) Marine Biogenic Sulphur

By far the largest contributor to the sulphur budget is the biogenic, marine source, with estimates of 45% of sulphur found in the southern hemisphere being biogenic in origin [Bates et al, 1992]. Non sea salt sulphate and MSA are the end products of an oxidation series of various gaseous sulphur bearing compounds, produced by biogenic activity. Biogenic sulphate and sulphur are produced by marine phytoplankton, initially emitting dimethylsulphoniopropionate (DMSP), which in turn breaks down to dimethyl sulphide (DMS) in the oceans. Of the biogenic sulphur species found in Antarctica, DMS accounts for 90% of the sulphur input. The remaining 10% comprises hydrogen sulphide, carbon disulphide, dimethyl disulphide and methane thiol [Bates et al., 1992(b)].

The main algae producers of DMSP are the groups Dinophyceae and Prymnesiophyceae [Keller et al., 1989]. These are both chromophyte algae; species possessing chlorophylls. The production of DMSP will be highly dependent on the prevailing concentrations and species of chromophyte algae in an area. Other factors also influence the production and release of DMSP. During the austral autumn, as sea ice builds up, the absence of light and the relatively low salinity of ice (with respect to sea water), leading to higher density brine, creates a situation of enhanced vertical mixing in the ocean. These factors create unfavourable conditions for biological activity, and consequently lead to a build up of nutrients during the winter. With the onset of spring and the melting of sea ice, a build up of a low salinity layer above high salinity sea water occurs, resulting in limited vertical

mixing. Together with the recovery of light, the unmixed water and high nutrient levels, favourable conditions for phytoplankton to build up are created [Minikin et al., in press]. In section 3.9a we will see that nss-SO_4^{2-} has its maximum concentrations during the summer months, when phytoplankton growth is at its most prolific.

The release of DMSP, and subsequently DMS from marine algae, is thought to occur either when phytoplankton are grazed by zooplankton [Dacey and Wakenham, 1986], or through cleavage (catalysed by enzymes, and also producing acrylic acid) towards the end of the phytoplankton's life cycle [Ayers, et al., 1991; Turner et al., 1988].

Once DMS is produced it escapes into the atmosphere by air-sea exchange, through transfer into the air via bubbles and waves at the ocean surface. As DMS is relatively insoluble and unreactive in sea water, processes on the water side of the air-sea interface control its rate of loss from the oceans. The liquid viscous boundary layer thus provides the largest resistance to DMS release [Liss and Galloway, 1993]. Concentrations of DMS in air are found to be elevated during episodes of high winds and overcast skies. The transfer velocity, as a function of wind speed, has been parameterised, with the two most widely used calculations being that of Wanninkhof, [1992] and Liss and Merlivat, [1986]. Increased concentrations during stormier weather are thought to be the result of faster air-sea exchange and less breakdown of DMS in the absence of sunlight [Andreae et al., 1985].

Once in the atmosphere, DMS is oxidised to methanesulphonic acid (MSA) and sulphur dioxide, by OH or NO_3 radicals. This oxidation process, described elsewhere in detail

[Barone et al., 1996; Turnipseed et al., 1996], is complex, but depends on atmospheric concentrations and temperature.

Further oxidation of SO_2 then occurs, to produce the condensed phase of hydrated sulphuric acid, and hence sulphate particles. Aqueous sulphuric acid may also be produced through binary nucleation of existing $\text{H}_2\text{SO}_4^{2-}$ and water molecules [Shaw, 1989].

Minikin et al., [in press] estimated that for coastal Antarctica between $17\text{--}50\text{ ng m}^{-3}$ of sulphate could be attributed to a winter background value; a non-DMS non sea salt sulphate signal, in coastal Antarctica. This background value is thought to be due to long range transport from volcanic, terrestrial and stratospheric sources.

A summary of the key stages in biogenic sulphur production is shown in figure 3.13.

3.8.b(ii) Volcanic Sulphur

Sulphur gases are also emitted by erupting and degassing volcanoes, with violent eruptions acting as the major sulphur source to the stratosphere [Pinto et al., 1989] These gases react to produce particles, the most important being sub-micron droplets of sulphuric acid [Shaw, 1989]. Sulphur dioxide is the primary species emitted, with particulate sulphate and hydrogen sulphide as secondary products. After entering the stratosphere, by upward transport, SO_2 remains there long enough for concentrations to become homogenized over both hemispheres. Residence times of gases and subsequent particles from large eruptions are particularly long and persistent. The particles eventually subside into the troposphere,

where they can be detected in aerosol sampling campaigns. It is estimated that less than 20% of the total sulphate deposited in Antarctic ice is stratospheric in origin [Legrand, 1995].

Volcanic activity is characterised by a sudden increase in sulphate concentrations in air and snow, often lasting for several years [Delmas and Boutron, 1980]. This eventually results in sulphate bands in ice cores. For example, the following eruptions have been detected in Antarctic ice: Deception in 1641, Tamboura in 1816, Krakatoa in 1883 and Agung in 1963. (For more detailed information on volcanic activity and references therein, see Cole Dai, et al., [1997]; Delmas et al., [1985] and Delmas and Boutron [1980]). However, these sulphate signals are not always easily identified as volcanic in origin, and are only recognised by a sudden, unexpected and short lived increase in concentration. This subjective method is particularly difficult for minor eruptions, where the sulphate signal may not be as strong.

3.8.b(iii) Continental Sulphur

Continental sulphur input is generally in the form of calcium sulphate, formed by reaction of non sea salt sulphate and calcium carbonate particles. As both calcium and sulphate have other sources, this component can not be measured directly and therefore can not be directly linked to a continental source. However, radioisotopes such as ^{210}Pb , originating from ^{222}Rn found in terrestrial dust, can be used instead to act as a tracer for air masses that have come in contact with land at some point.

A limited number of studies have been made in this field. ^{222}Rn has been measured off the northern tip of the Antarctic Peninsula, in the Southern Drake Passage and Gerlache Strait, by Pszenny et al., [1989]. ^{210}Pb has also been monitored at Neumayer station by Wagenbach et al, [1988]. In both cases very low, but measurable, mineral aerosol and radioisotope concentrations were found, indicating that the sampled air did have some continental character. This implies that continental sulphur could indeed have a small influence in Antarctica. However, CaSO_4 particles are typically larger than $1\text{ }\mu\text{m}$, making the possibility for long range transport more difficult [Bates et al., 1992b].

Aerosol calcium concentrations at Halley are so low that they imply a limited influence of CaSO_4 on the total sulphate budget at this coastal Antarctic site (see figures 3.1 and 3.2). (The maximum mean monthly calcium concentration is just 6 ng m^{-3}). Bearing in mind that the majority of this calcium will be sea salt in origin, any continental contribution is likely to be minimal.

3.8.b(iv) Anthropogenic Sulphur

Sulphur from anthropogenic sources is mainly in the form of sulphur dioxide, produced from the combustion of fossil fuels. Over the last 100 years ice cores from south and central Greenland have shown a significant increase in sulphate concentrations [Mayewski et al., 1990; 1986; Neftel et al., 1985]. This increase in sulphate has also been found to follow the trend in SO_2 emissions from the United States [Mayewski et al., 1990]. It is clear that the sulphate increase reflects the increase in fossil fuel burning and is due to long range transport of pollution from mid and high northern latitudes.

However, a similar increase in ice core sulphate concentrations has not been observed in Antarctica [Legrand, 1995]. This is partly because of restricted transport due to air mass circulation patterns that exist around Antarctica, but also because only a small portion of total global biomass and fossil fuel burning occurs in the southern hemisphere. It is estimated that only 10% of anthropogenic sulphur emissions actually occur in the southern hemisphere [Bates et al., 1992b].

The main pollution in Antarctica is that from scientific research stations, where diesel is used to power vehicles, and for heat and power generation. This effect tends to be very localised [Bouton and Wolff, 1989] and therefore we can assume that the anthropogenic influence on Antarctica at the present time, is minimal. This assumption is backed up by aerosol black carbon measurements collected between 1992 and 1995 at Halley, using an aethalometer. Particularly high spikes of black carbon were compared with the corresponding aerosol sulphate record (figure 3.14 and section 2.8). It was found that even during the highest black carbon events no perturbation could be detected in the sulphate record. This results confirms the theory that contamination from research stations, is very localised and in the case of Halley does not seem to affect aerosol concentrations.

3.8.c Significance of Biogenic Sulphur Species

The sulphur cycle is one of the most important biogeochemical cycles which affects the atmospheric composition of the Earth. The end products of a series of oxidations of reduced sulphur species contribute a large proportion of acidity to the atmosphere. Sulphur

gases, converted into sub-micron sulphate aerosols, have the potential to interact with incoming solar radiation and could affect the global climate.

DMS emissions from phytoplankton dominates the production of cloud condensation nuclei (CCN) over the oceans [Bates et al., 1987]. An increase in DMS concentrations, would increase the concentration of nss sulphate aerosols. This could then increase CCN population in clouds [Charlson et al., 1987]. This would result in the formation of more small droplets in the cloud, increasing its reflectivity to sunlight, and increasing the cloud albedo. The effect would be to decrease incoming, incident solar radiation at the Earth's surface, which in turn would effect production of DMS in the oceans [Shaw, 1983] and result in a negative climate feedback mechanism [Charlson et al., 1991; 1987]. Therefore, DMS emissions, and subsequently nss sulphate and MSA concentrations, could be used as a link to the climate and biological activity of past and present oceans. As the only atmospheric source of MSA is the oxidation of DMS, this makes it a particularly important species to study.

3.8.d Determination of Non Sea Salt (or excess) Sulphate

Non sea salt sulphate (or excess sulphate) is calculated by subtracting the sea salt sulphate component from the total sulphate concentration measured in the samples, ie:

$$[\text{Total SO}_4^{2-}] - [\text{sea salt SO}_4^{2-}]$$

This can also be written as:

$$[\text{nss SO}_4^{2-}] = [\text{SO}_4^{2-}]_{\text{total}} - k[x]$$

where x is the reference sea salt component, usually sodium (or chloride), and where k is the respective bulk sea water ratio (BSW), $[\text{SO}_4^{2-}]/[\text{Na}^+]$. As already described earlier in this chapter, in section 3.5, the traditionally used bulk sea water ratio of 0.252 for sodium, can not be used for most of coastal Antarctica, particularly during the winter. This is due to a significant fractionation of the sea salt component, resulting in a deficit of sodium sulphate during the winter months, when temperatures drop below -8.2°C . If 0.252 is used as the bulk sea water ratio, a large number of calculated nss sulphate values, during the winter, become negative.

In section 3.5, it was shown that at Halley, (for aerosol sea salt concentrations based on sodium), a bulk sea water ratio of 0.107 should be used. Earlier work by Wagenbach et al., [in press] used a BSW ratio of 0.075, an average of corrected BSW ratios from Halley, Neumayer and Dumont D'Urville. However, it seems prudent to use a ratio which matches the level of fractionation occurring at a particular site. In the case of Halley this is 0.107 (see figure 3.8), and is the bulk sea water ratio used whenever aerosol nss sulphate is referred to in this thesis as the corrected value. Figure 3.15 shows nss sulphate values calculated in the traditional way, using 0.252 as the BSW ratio and the corrected Halley record, using BSW ratio of 0.107. The negative values obtained using BSW ratio of 0.252 are clearly seen and can be up to -100 ng m^{-3} in the worst case.

Although fractionation is most prevalent during the winter, this ratio can also be used during the summer months at Halley. In figure 3.15 the difference between the two plots during the summer can be seen to be minimal. This is because the sea salt signal at Halley

is weak during the summer and therefore the presence or absence of fractionation only slightly influences the calculated non sea salt sulphate concentrations. Also, temperatures at Halley during the summer can still fall below -8.2°C , the temperature below which fractionation is expected to occur [Wagenbach et al., in press]. This would not be the case for every Antarctic station. For instance, at Dumont D'Urville the summer sea salt signal is very strong, and warm temperatures, together with the absence of sea ice, are likely to result in no fractionation at all during the summer. At Dumont D'Urville, using a corrected bulk sea water ratio during the summer would lead to an increase in non sea salt sulphate estimated at about 50% [Minikin et al., in press], because the nss SO_4^{2-} level here is strongly dependent on the BSW ratio used.

3.9 Seasonality of Sea Salt Sulphate

Figure 3.16 shows the daily, raw data for corrected non sea salt sulphate and methanesulphonic acid at Halley. Figure 3.17 are the same data, but displayed as monthly averages.

3.9.a Monthly Variability

The seasonal cycles of MSA and nss sulphate both clearly peak during the austral summer, with a broad winter minimum. Many other stations report the same seasonality [Minikin et al., 1994; Mosley-Thompson et al., 1991; Tuncel et al., 1989; Mulvaney and Peel, 1988; Wagenbach, 1988]. The summer maximum is due to marine biogenic input from sulphur

producing oceanic phytoplankton [Ayers et al., 1991; Mulvaney and Peel, 1988; Wagenbach 1988; Shaw, 1988]. Both MSA and nss sulphate seasonal cycles follow that of oceanic, biogenic sulphur producers, with DMS as the seasonal indicator. Figure 3.18a shows atmospheric DMS measured at remote site Cape Grim, Tasmania and 3.18b, from Neumayer station, Antarctica. (NB: The atmospheric DMS signal for Neumayer is based on one years data, and should therefore be treated with caution). Both these time series show DMS peaking during the summer months, suggesting a strong link with MSA and nss sulphate, which also peak during summer. However, elevated atmospheric DMS at Neumayer (fig. 3.18b) is also found during winter, with rapid concentrations changes. Such sudden variations in DMS concentrations during winter cannot be attributed to a change in DMS sources strength, since the marine biological activity is already insignificant at that time of year in regions located south of 60°S. Instead the concentrations seem likely to reflect an overall seasonal cycle of DMS, with long range transport possible in winter, due to low concentrations of oxidant species (OH) at that time of year and in these regions of the southern hemisphere [Minikin et al., in press]. Figure 3.18b also shows that summer DMS concentrations begin to increase in December, a few months later than the increase seen in aerosol nss sulphate and MSA at Neumayer (fig 3.19). DMS concentrations are enhanced by an order to magnitude from December to January, whilst nss sulphate and MSA increase by only 30% and a factor two, respectively.. This suggests that local emissions do not dominate the overall sulphate and MSA inputs in mid-summer.

Using satellite imagery of chlorophyll concentrations, Minikin et al., [in press] have determined that marine source regions available to Halley, during the summer (November

to May), are likely to come from between 60°S and the continent's edge. During the winter (May to August), no marine biogenic activity takes place south of 60°S, determined by chlorophyll concentrations close to zero. Between May to August, longer range transport dominates and marine source regions will tend to be available most from 50-60°S and north of 50°S, due to larger extent of sea ice.

The variations in aerosol non sea salt sulphate concentrations are well explained by changes in the chlorophyll content of the ocean. Figure 3.19 shows the nss sulphate cycles for four bases (including Halley) and also corresponding chlorophyll concentrations at various degrees south. In this plot nss sulphate mirrors the chlorophyll concentrations. However, the correlation between DMS and chlorophyll is not always this good and reflects the fact that DMS production is strongly dependent on algae speciation, with some species being more prolific. It therefore seems likely that in the marine area around Halley, and the other bases shown in figure 3.19, the dominant algae source must be that which produces both DMS and chlorophyll. This is likely to be a species such as Dinophyceae, or Prymnesiophyceae [Keller et al., 1989].

The highest concentrations at Halley are found during February, where mean monthly MSA concentrations are 42 and 76 ng m⁻³ in the two years, and 137 and 203 ng m⁻³ for non sea salt sulphate, (see table 3.2). This February maximum is a month later than that seen in records at Neumayer, Dumont D'Urville and Mawson. At these stations the peak is found during January. This later increase can be linked to the delay in sea ice retreat at Halley, compared to the other stations. During the winter months, May to August, MSA values are

often less than the detection limit of 2 ng m^{-3} .

In table 3.2, the virtue of using corrected non sea salt sulphate concentrations during the winter months is highlighted. Corrected values range from $4\text{--}18 \text{ ng m}^{-3}$, in comparison to the non corrected values which are zero or negative.

Table 3.2: Mean monthly concentrations for MSA, corrected nss sulphate (calculated using BSW ratio 0.107) and traditional nss sulphate, shaded in grey and shown for comparison only (calculated using BSW ratio 0.252). The standard deviations are also shown. In some cases negative and zero values are shown, particularly during the winter months, when concentrations are often below the detection limit.

Month	MSA Avg/ ngm^{-3}	MSA Std	Corr. nss SO_4^{2-} Avg/ ngm^{-3}	Corr. nss SO_4^{2-} Std	nss SO_4^{2-} Avg/ ngm^{-3}	nss SO_4^{2-} Std
feb 91	42	20	203	99	198	96
mar	34	57	113	57	107	9
apr	8	24	27	23	19	9
may	0	0	15	30	10	23
jun	0	1	4	15	-7	21
jul	0	0	9	19	-3	18
aug	0	1	7	12	-2	27
sep	1	1	26	16	20	16
oct	1	1	22	18	19	17
nov	1	2	26	14	26	14
dec	6	7	36	25	35	25
jan 92	13	9	52	24	55	20
feb	76	53	137	53	134	53
mar	61	49	97	66	92	65
apr	11	12	22	21	26	18
may	0	1	18	10	15	10
jun	0	1	11	7	3	20
jul	0	2	11	10	0	21
aug	1	1	15	9	2	25
sep	4	2	21	11	6	20
oct	4	2	30	15	23	16
nov	4	2	36	17	31	15
dec	22	26	73	49	60	41
jan 93	54	38	138	72	124	66

3.9.b Annual Mean Concentrations: in comparison with other reported Antarctic aerosol records

The annual mean for methanesulphonic acid aerosol concentration at Halley is 15 ng m^{-3} and 49 ng m^{-3} for corrected non sea salt sulphate. As with the sea salt species examined earlier, these values are relatively low in comparison with other reported, continuously sampled, MSA and nss sulphate aerosol values in coastal Antarctica. Neumayer station, facing the Atlantic Ocean, has an annual mean for MSA of 38 ng m^{-3} and for corrected nss sulphate, 151 ng m^{-3} [Minikin et al., in press]. For Mawson, on the eastern coast of Antarctica, MSA is 23 ng m^{-3} and nss sulphate is 90 ng m^{-3} [Savoie et al., 1993]. The value for nss sulphate has since been recalculated, using 0.07 as BSW ratio by Minikin et al., [in press], and changes to 111 ng m^{-3} . In general, caution should be used when comparing non sea salt sulphate values. Non corrected data sets may give a lower than actual annual mean due to a significant number of lower (and even negative) values, particularly during the winter. Other reported concentrations are shown in table 3.3.

Table 3.3: Summary of MSA and non sea salt sulphate aerosol concentrations.

Conc. in ng m^{-3}	Halley	Neumayer	Mawson	Dumont D'Urville	Marsh	Palmer	South Pole
MSA	15	38	23	20 ¹	30 ²	49 ³	--
nss SO_4^{2-}	49	151	111 (90) ⁵	147	--	(97)	(74) ⁴

¹[Minikin et al., in press]

^{2 and 3} [Savoie et al., 1993]

⁴[Tuncel et al., 1989]

⁵Non sea salt sulphate values in parenthesis indicate that they have been calculated using the traditional value for the bulk sea water ratio, BSW = 0.252.

Differences between MSA and nss sulphate concentrations at Halley, compared to other

Antarctic stations, are similar to those differences already discussed in section 3.3, with regard to sea salt. The main reasons for a lower nss sulphate and MSA annual mean are Halley's location and local climatology. Halley is located 4° further south than Neumayer, resulting in a greater distance between the coast and the maximum sea ice edge during the summer. In comparison with Neumayer station, air reaching Halley has travelled a further 500 km south, without definitely passing over open water [Simmonds and Jacka, 1995], (table 3.4). At Neumayer the open water fraction reaches its maximum of 100% in January [Minikin et al., in press]. At Halley this 100% open water fraction never occurs, allowing MSA and non sea salt sulphate concentrations to continue increasing up to their February maximum, a month later than Neumayer.

Table 3.4: Distance of Halley and Neumayer from the ice edge during the Austral summer.

	December	January	February
	Distance from ice edge /km's		
Halley	1260	600	240
Neumayer	800	180	60

NB: Adapted from Simmonds and Jacka, [1995].

Also, as already discussed, the predominant wind direction at Halley is easterly, from inland and without contact with the ocean and sulphur producing algae. Approximately 40% of the winds occur directly from the east and 30% from north and south east [Hanssen-Bauer, 1992]. At Neumayer, where sulphate concentrations are considerably higher than Halley, the predominant easterly winds pass directly over open water only 6.5 km away, before

reaching the station [Wolff et al., in press]. The nearest open water to the east of Halley, is the Ross Sea, on the opposite side of the Antarctic continent. There is therefore no readily available source of sulphate particles east of Halley. Even in the less common westerly - west south west direction (where winds occur between 4-13% of the time depending on the season [Hanssen-Bauer, 1992]), Halley is some 15 km from the ice shelf edge. For more detailed information on the climatology of Halley refer to section 1.5b, also König-Langlo et al., [in press] and Hanssen-Bauer, [1992].

The Halley data set for MSA and nss sulphate also lacks some key dates for calculating an annual mean. These are from 20 January 1992 to 13 February 1992, missing summer values, when concentrations of these species would be at their highest. This lack of data is due to the relocation of Halley base, a further 15 km inland, and the subsequent period of disruption for the over-wintering meteorologists who collected the samples for this project.

There is also the possibility that some non sea salt sulphate may be attributable to eruptions from Cerro Hudson and Pinatubo, affecting concentrations between November 1991 and October 1992. This has been observed in the Dumont D'Urville and Neumayer data sets between 1991 and 1992 and also elevated concentrations were seen in Spring 1991 at Mawson. Due to the shorter time scale of the Halley data it is difficult to assess whether the concentrations seen for nss sulphate are unusually high.

3.9.c MSA to Non Sea Salt Sulphate Aerosol Weight Ratio, $\text{MSA}/\text{nss SO}_4^{2-}$, (or R).

Early reports of Antarctic MSA to nss sulphate weight ratios (R) suggested that, due to its consistency, it could be used as a marker for the fraction of nss sulphate attributable to biogenic DMS [Savoie and Prospero, 1989]. Unfortunately, R has since proved less than conservative and factors that may control it, such as temperature, light intensity, or oxidant concentration, are not well understood. For instance, it is thought that R values are dependant upon temperature and could therefore be used as a latitudinal tracer. R was found to be greater, of the order 50%, at higher latitudes [Pszenny et al., 1989; Saltzman et al., 1983]. Bates et al., [1992] found that the ratio had an inverse relationship in the marine boundary layer, as a function of latitude, with high ratios suggesting a high latitude marine source.

However, the inverse relationship between R and temperature appears not to hold true, as highest chemical concentrations of MSA and nss sulphate are found during the summer - the warmest months (see figure 3.20). This can be explained because during the winter the DMS source, and thus the source of MSA and nss sulphate, is north of 60°S [Minikin et al., submitted], during the summer, the source is closer to Antarctica. The further north the DMS source is, the warmer the atmosphere becomes. This effectively means that DMS produced during winter is done so in air temperatures warmer than when DMS is produced south of 60°S [Legrand and Pasteur, in press]. In other words, the summer source may be colder than the winter DMS source. This being the case, more MSA is produced when the temperatures are colder, reinforcing the theory that R is inversely proportional to

temperature. The dependence of R on temperature is still controversial and is discussed in more detail elsewhere, [Ravishankara et al., 1997; Bates et al., 1992].

It is clear that the MSA/nss sulphate ratio, and the factors controlling it, are complex. Apart from the factors already mentioned, we can not be 100% sure that the sea salt fractionation process (see sections 3.5 and 3.8d) occurs for every sample. This is not likely to affect the overall annual mean R, but on a day to day basis examining the ratio becomes difficult. Figure 3.21 shows R plotted using non sea salt sulphate calculated using corrected and traditional values of the bulk sea water ratio. From this plot we can see that the main feature, a February maximum, is unaffected by altering the nss sulphate values.

At Halley the seasonal cycle of R, although weak, peaks during the summer with highest concentrations during February, (the same pattern as the seasonal cycle for the individual species) (see figure 3.21). Ratios are lowest during winter, however it should be reinforced that the winter R values are, in some cases, meaningless if calculated with negative concentrations. Ratios for individual days are often noisy, and it is clearer to look at monthly means (see table 3.5). The annual mean MSA/nss SO_4^{2-} ratio for Halley, calculated as the mean ratio for individual days, is 0.12. This is comparable to ratios found at Neumayer of 0.18 and at Dumont D'Urville of 0.12 [Legrand and Pasteur, in press]. However, if MSA values which are less than the detection limit of 2 ng m^{-3} are removed from the data set, the ratio at Halley increases to 0.27. Exclusion of these values changes the emphasis of the annual mean, making it less influenced by the low (and sometimes negative) winter values. This new mean is more comparable with that found at Mawson

station, of 0.22 [Prospero et al., 1991].

Table 3.5: Average aerosol MSA/nss SO_4^{2-} monthly ratios for Halley. The shaded area represents winter values, these are calculated using MSA concentrations which are often less than the detection limit and should therefore be treated with caution.

Month	MSA/nss SO_4^{2-}	Month	MSA/nss SO_4^{2-}
feb 91	0.22	feb 92	0.51
mar	0.16	mar	0.59
apr	0.23	apr	0.25
may	0.01	may	0.01
jun	-0.15	jun	-0.10
jul	-0.22	jul	-0.07
aug	0.09	aug	0.05
sep	-0.09	sep	0.20
oct	-0.31	oct	0.20
nov	0.07	nov	0.11
dec	0.15	dec	0.06
jan 92	0.24	jan 93	0.36

3.9.c(i) Non Biogenic Non Sea Salt Sulphate

In order to identify any non biogenic non sea salt sulphate component in the Halley aerosol samples, nss sulphate is plotted versus MSA (Figure 3.22). Any non zero y-intercept will suggest a non DMS source for nss sulphate. This is because MSA concentrations have DMS emissions as their sole atmospheric source. For both summer and winter, the non sea salt sulphate and MSA are well correlated. During winter, the y-intercept is 13 ng m^{-3} and could be attributable to a non biogenic nss sulphate source. This is comparable to values calculated for Mawson and Neumayer of 20 ng m^{-3} [Minikin et al., submitted]. However, it is also possible that the sea salt fractionation process (see sections 3.5 and 3.8d) may be overestimated and the corrected bulk sea water ratio used to determine nss sulphate

concentrations may be too low. During the summer, the y-intercept is 34 ng m^{-3} (comparable with Neumayer and Mawson value of $20\text{-}25 \text{ ng m}^{-3}$ [Minikin et al., in press]), but represents only a small proportion of the total nss sulphate amount.

It should also be noted that plot 3.22 assumes that real R is constant for biogenic sulphur, throughout the year. This implies that no curvature exists in the line. However in practice, during the summer curvature may exist, rendering this procedure for estimating a background value, void.

3.10 Daily Variability in MSA

The daily sampled nss sulphate and MSA aerosol record at Halley (figure 3.16) gives us the ability to look at individual, high concentration events in detail, with the aim of validating the source of these species. Previous sampling campaigns, although often over a longer time period than that of Halley, have collected samples weekly or fortnightly, making it difficult (if not impossible) to confidently attribute features in the meteorological record to increases in concentration. The Halley data will be used in conjunction with local meteorological records and longer range back trajectory modelling (see section 3.11), to attempt to validate the region and source of MSA and nss sulphate, particularly during the summer maximum. As already discussed (see sections 3.9a), this source in summer is thought to be mainly, long range transport of DMS emissions from marine phytoplankton algae. As DMS is the sole source of atmospheric methanesulphonic acid, it is this component that is now studied in detail.

Using the Halley daily aerosol data it is possible to see that the strong summer maximum is controlled by the occurrence of a few specific, high events in the data set. In comparison with the sea salt individual events, MSA high concentrations are not as obvious and tend to gradually increase in concentration, rather than suddenly spike. Concentrations can increase by a factor 30 over such events, but generally no more than a factor 9 between days. Eight events of the highest variability are investigated during the summer months.

3.10.a Local Conditions

Figure 3.23 shows these plots and also the corresponding wind speed and direction over the period. Unlike the case for sea salt, there appears to be no obvious correlation between MSA concentrations and local wind speed and direction. Figure 3.23 shows that wind speed does not change significantly on the day of highest concentration, compared with the previous day. However, the speed does tend to stay below 10 ms^{-1} throughout these events and suggests that they are not characterised by especially high wind speeds.

Three events clearly experience a change in wind direction, from easterly (over inland) when low in concentration, to westerly (from over the sea) on the highest concentration day (February -March, 21-26 December 1992 and 1-4 January 1993). Another three events also exhibit this behaviour, however, the wind only 'dips' west on the day of high concentration (February, 9-14 December 1992 and 3-10 January). These scenarios seem logical, with an easterly wind opening up an area of water, switching to a westerly, which brings MSA and nss sulphate inland, if the source is a local one. The wind direction would theoretically,

only need to dip west for a short period in order to bring these particles inland.

The remaining 2 events (5-11 March and 9-13 March 1992) are westerly (from over water) before the highest concentration day, then dip easterly (from inland) and westerly (from over water), before returning to easterly again. As these high events are all summer ones it is conceivable that open water already exists and an easterly is not required to open up the sea ice. This being the case, the only requirement, just before a high concentration event, is a westerly wind to bring particles from the ocean to inland.

Average MSA and nss sulphate concentrations were also plotted against frequency of local winds in a particular direction over the year, figure 3.24. As described in section 1.5.b(iii), local winds at Halley generally come from the east, with the secondary direction as westerly. Figure 3.24 shows that both MSA and nss SO_4^{2-} generally follow the same trend, when plotted against corresponding wind direction. Lowest MSA and nss sulphate concentrations are associated with easterly winds and highest concentrations with westerlies. This is generally true, apart from 20 days when winds came from the $140\text{--}160^\circ$ sector. For this direction nss sulphate concentrations were slightly elevated, in comparison with MSA and could indicate a non biogenic non sea salt sulphate source during this period. However, for these 20 days MSA was available for only 12 days out of the total 20, whereas non sea salt sulphate was measured on every day. This could have the effect of masking, or missing out, any high MSA values.

Average MSA and nss sulphate concentrations were replotted, with particular wind

directions, but for the summer months only (figure 3.25). This is necessary in order to show that the plot is not driven by a seasonal wind direction dependence. Low concentrations during easterly winds and high values during westerlies could simply indicate that more easterlies occur in the winter, when MSA is low anyway. Figure 3.25 eliminates this possibility, showing that even during the summer months, when biogenic sulphate concentrations are at their highest, a similar pattern is found with low concentrations occurring during easterly winds, from inland.

It is clearly not easy to interpret, with confidence, these local wind speeds and direction signals with respect to nss sulphate and MSA concentrations. The most conclusive comment would be that local meteorology has a limited influence on biogenic marine sulphur concentrations.

Further validating the thought that the source of MSA and nss sulphate is not a local one is the fact that concentrations decrease far more slowly, in comparison with sea salt, with distance from the coast [Mulvaney and Wolff, 1994]. Minikin et al., [1994] found that 100 km inland, sea salt had decreased in concentration by 50%, whereas nss sulphate was only depleted by 10%, again implying a non local source for this latter species. Even more compelling evidence is that Legrand and Delmas [1985] found that over a 430km coast-interior traverse in East Antarctica, nss sulphate concentrations in fact remained the same throughout the length of the journey. Figure 3.26 demonstrates the rapid decline in sea salt concentrations and the slower, more gradual decrease for MSA and nss sulphate with distance inland, from the coast.

If local weather conditions do not influence the concentrations of MSA and nss sulphate found in aerosol at Halley then instead, longer range transport and weather patterns must dominate. This is in agreement with detailed work by Minikin et al., [submitted]. König-Langlo et al., [submitted], found that local wind direction and speed had no bearing on the origins of the air, on arrival at Neumayer. Clearly, longer range analysis is needed to pinpoint the true nature of the air reaching Halley during these individual episodes of elevated nss sulphate and MSA concentrations.

3.11 Regional Conditions: Back Trajectory Analysis

3.11.a Introduction

Back trajectories describe the pathway of infinitesimal air parcels through the atmosphere, ultimately, identifying the origin of the air mass. In polar regions, they have been used in several studies as a means to explain the concentrations of specific chemical aerosols. Davidson et al., [1985] used a 3 dimensional model [Olsen et al., 1978] to compute daily, 5 day back trajectories at Dye 3, Greenland, for a 2 month period. Each trajectory was individually inspected and categorised according to which region of the Arctic the air mass originated. Worthy et al., [1994] used the same model [Olsen et al., 1978] to compute 5 day, daily trajectories for Alert, Canada, from January to April 1992. The trajectories were calculated every 6 hours, at 4 pressure levels and grouped according to six geographical sectors. Major events in the chemical aerosol data set were then characterised according to their air mass origin. Wyputta [1997] used a 2 dimensional model, run at 3 pressure

levels, to explain specific events in the aerosol record at Neumayer station, Antarctica. Trajectories were manually grouped according to three common flow sectors at Neumayer; easterly (marine), easterly (continental) and westerly. Kahl et al., [1997] used 10 day isobaric back trajectories to compare with ground level aerosol measurements at Summit, Greenland, and to examine the link between air source regions and aerosol concentrations. Kottmeier & Fay [in press] used a 3 dimensional model to characterise air mass transport in the Atlantic sector of the Antarctic, in general terms. The work used a statistical approach to identify the trajectory origins, according to latitudinal sectors.

The aim of this work is to provide general trends in the origin of air masses reaching Halley, for specific events of high concentration in the aerosol data record. Back trajectories were run from days when the concentration of aerosol methanesulphonic acid and sea salt, measured at Halley, was found to be high. These episodes of high concentration have previously been studied, along with local meteorological events in sections 3.4 (sea salt) and 3.10 (MSA). A full account of the results can be found earlier in this chapter. Briefly, MSA appears to have no direct link to the local meteorological events at Halley. This indicates that the source for MSA is a non local one, whereas high concentrations of aerosol sea salt do coincide with particular local meteorological conditions. For this species, high values are associated with a wind direction pattern that could have opened an area of local water, bringing any sea salt particles produced inland, with the subsequent change in wind direction. The source of aerosol winter sea salt is therefore thought to be a local one. In both cases, longer range air mass origin analysis is required for a clearer understanding of the sources for these two species.

3.11.b The Trajectory Model

The back trajectory model was run by Steven Leonard of the British Antarctic Survey, and his help is acknowledged here.

The data used to calculate back trajectories of air parcels arriving at Halley, are obtained from the European Centre for Medium-Range Weather Forecasts (ECMWF). Three dimensional velocity fields are used, two horizontal and one vertical. The horizontal component comprises wind speed (in ms^{-1}), in the zonal (west to east) and meridional (south to north) directions. The vertical co-ordinate used is pressure and hence the velocities are in pascals s^{-1} . The velocity data are from the re-analysis project, carried out at ECMWF, which produced a consistent set of analyses for a 15 year period, 1979-93. The analyses are a combination of actual observations and a 6-hourly background forecast, produced by the assimilation scheme used in the re-analysis project. (More information on the re-analysis programme and data available, can be found in ECMWF, [1996]). The velocity fields are given on a series of standard pressure levels, with 15 levels, ranging from 1000 hPa to 10 hPa. The model operates on a 2.5° resolution grid, which corresponds to about 200 km horizontally. The data-set also has a temporal resolution of 6 hours, with data available for 00Z, 06Z, 12Z and 18Z. For this project back trajectories were calculated starting from the 900 hPa level, as it is between this level and the surface that aerosol sampling takes place at Halley. Also, only back trajectories corresponding to air parcels arriving at Halley at 12Z were investigated.

The actual back trajectory model is a FORTRAN programme from the British Atmospheric Data Centre (BADC), developed at UK Universities' Global Atmospheric Modelling Programme (UGAMP) [Methven, 1997]. The programme works by integrating the velocities for the 3D co-ordinates, longitude, latitude and pressure, using a fourth order Runge-Kutta method [eg. Press et al., 1986]. Velocities are calculated at intermediate points by linear interpolation in the horizontal and third order polynomial interpolation in the vertical. The programme calculates the surface pressure by interpolating the height of the standard pressure levels, (also obtained from BADC), based on the model surface topography, used in the re-analysis project. For this work, the back trajectories were stopped if they hit the model surface.

The main trajectories were run back from Halley research base ($75^{\circ}35'S$, $26^{\circ}19'W$) for 5 days and also from 4 neighbouring locations (N,S,E,W), at 1° distances around Halley. The availability of these 5 trajectories, run from similar locations, enables us to examine the consistency of the model's predictions (see section 5.11.d).

3.11.c Trajectory Classification

The aim of this work is to identify any general trends in the origin of air masses reaching Halley, when there are high concentrations of aerosol MSA and sea salt. Since both these species originate from marine sources, it is especially important to differentiate trajectories

passing exclusively over land and those passing mainly over water. As a result, the chosen back trajectory classification for this project, groups air parcels according to whether they passed over water or land. The trajectories were manually sorted into 4 categories, and these were:

Cc	Continental coastal
Ci	Continental interior
Mo	Marine open water
Mc	Marine coastal

Continental coastal (Cc) describes a region of continent, or permanent ice shelf, which is bordered by the coastline and is no greater than 5° of latitude inland (see figure 3.27). Any trajectory falling outside this 5° envelope is categorised as continental interior (Ci). Ci could also include permanent ice shelf, such as areas of the Filchner Ronne (see figure 3.27). Marine coastal (Mc) is the area of ocean which falls between the coastline and 5° of latitude seaward (see figure 3.27). Marine open water (Mo) is any area of ocean outside this 5° envelope (see figure 3.27).

Trajectories are also classed according to their altitude. Simply, in tables 3.6 and 3.7, trajectories between the 850 hPa pressure level and the surface are marked in red. An air parcel's altitude is relevant, as it will give an indication as to the likelihood of air being low enough to actually collect sea salt, or MSA aerosols, which are produced at ground level. (It should be noted that day one will always have a trajectory that travels between 850 hPa and the surface, because the model is run from the 900 hPa level to begin with).

3.11.d Consistency of Trajectory Model

Complete validation of the trajectory model would require forward trajectories, run from the predicted origin of the air mass. Verification could also be achieved against air mass tracer releases such as radioactive accidents, Kuwaiti oil fires and Saharan dust [Kottmeier & Fay, in press]. This was not undertaken in the scope of this work. However, the consistency of the results can be examined, by comparison of the four other trajectories run from 1° distances around Halley. As the model runs on a 2.5° resolution grid, trajectories run at 1° intervals around Halley should show similar air mass origins and pathways. If they do not, then the implication is that the particular trajectory is unreliable.

Of the four other trajectories run, 30% were placed in the same group classification as the Halley trajectory, after 5 days. This low percentage is usually due to one trajectory hitting the surface topography and therefore immediately stopping. However, if one trajectory is allowed to fall in a different sector (therefore 4 out of the 5 back trajectories ending in the same sector), then over 70% of the remaining trajectories do originate in the same sector as Halley. This can be seen in tables 3.6 and 3.7.

3.11.e Trajectory Results

For each specific episode the air parcel's predicted location, prior to the high aerosol concentration event, over 5 days is displayed in tabular format. The day (and in some

cases, days) of highest aerosol concentration is indicated by a shaded row, in tables 3.6 & 3.7. Day one, of the number of days the air mass is tracked back for, is one day from Halley. The sample date, is the day when the aerosol sample was collected and also the date from which the back trajectory model begins its analysis. The date junctions are marked on each trajectory by a cross.

Plots of the aerosol concentration for MSA during the specific events, can be seen in figure 3.23, and in figure 3.6 for sea salt.

3.11.f Methanesulphonic Acid Aerosol

Eight cases of high MSA were studied. In all but one case, the back trajectories indicate that the air parcel reaching Halley on the day of high concentration, did previously pass over an area of water. This can be seen in table 3.6, which shows a classification of either Mo or Mc for water, for the back trajectories run on the highest MSA concentration day.

Each event is now examined in detail, and also in conjunction with weekly, composite sea ice coverage charts [NOAA, 1991-92]. These are prepared using passive microwave imagery and direct observations. The charts have a resolution of around 50 km, and therefore do not show any areas of localised open water, or small leads. However, any open water that is indicated by the charts, is likely to be an accurate assessment of the conditions at the time. This is because open water features need to be larger than 50 km before they are detected and displayed. For this work, the charts are used to speculate on the

availability of open water when a trajectory is seen to pass over the ocean. The day of highest MSA concentration is indicated in brackets, after the event number below.

Event 1: (25 February 1992) The back trajectory on the day of high concentration clearly passed over the sea 3 days back from Halley (see figure 3.28). However, the trajectories for the day before (see figure 3.28), and the day after highest MSA, also pass over the ocean. On individual inspection, the air mass on the highest concentration day (25 February) extends further northward into the sea (and is classified as Mo), than on the 24. Concentrations remain elevated on the 26, and this corresponds to the trajectories position, which still extends further into the sea (Mo). Sea ice charts show that close to the coast there was indeed 90-100% sea ice coverage, but only slightly northward (and where the trajectory for the 25 February passes), the sea is ice free (see figure 3.29).

Events 2 and 8: (01 March 1992 and 06 January 1993) Trajectories run for these two events show the air mass passing over the continent (Cc or Co), both before and after the day of high concentration. The trajectories passed over water only on the actual day of high MSA. Event 2 came into contact with the ocean two days before reaching Halley, and event 8, just one day. In both cases, the pressure was greater than 850 hPa and therefore closer to the surface, enabling the air mass to efficiently collect any MSA particles produced. The sea ice coverage for the 01 March 1992 was between 10 and 50%, in the area of the trajectory. For the 06 January 1993 there are many patches of open water and less than 50% sea ice coverage.

Event 3: (07 March 1992) Trajectories run for the 07 March 1992 indicate that the air parcel travelled over the ocean 2 days prior to arrival at Halley. Weekly sea ice charts show that the area where the trajectory passes (close to Halley), is likely to have areas of open water, with a sea ice coverage of 20-40%. On the 8 and 9 March concentrations decrease and the trajectory travels mostly over land, briefly passing over sea which has a 90-100% ice coverage.

Event 4: (11 March 1992) For this event, the days before and after high concentration, have trajectories which extend well into the Weddell Sea and towards the Antarctic Peninsula (Figure 3.30). From Halley, on these days, the air mass reaches further northwards, over the Brunt Ice Shelf, before making contact with the sea. In doing so, it avoids a possible area of open water (20-40% ice coverage) close to Halley. The area of Weddell Sea it does pass over, is densely covered with ice (90-100%), making contact with open water unlikely. On the day of high concentration (11 March), the air mass moves much closer to the coastline, and travels over the Filchner Ronne Ice Shelf (Figure 3.30). This pathway offers 2 possible areas of open water, with an ice coverage of 20-40%, one of which flanks the Filchner-Ronne. Figure 3.31 shows the weekly composite sea ice coverage chart for this event.

Event 5: (12 December 1992) The two days preceding this event have trajectories which pass over land and sea. On the 10 December, the sea ice coverage in the trajectories path is 90-100%. On the 11 December, the sea ice coverage is somewhat uncertain, with 90-100% coverage in most areas, but patches of 30-50%. This latter percentage is, however,

an estimated value, and as a result must be treated with caution. The day of highest concentration, 12 December, has a trajectory which closely follows the coastline 2 days before reaching Halley. This region is dominated by a coastal lead, classified as 0% ice. Concentrations of MSA at Halley are low on the 13 December, and this ties in with the back trajectory which places the air mass origin over the continent.

Event 6: (23 December 1992) For event 6, when concentrations are low (21 and 22 December), the air is found to pass over land. The air mass arriving at Halley on the 23 December, previously travelled over the sea at low altitudes one day before reaching Halley. Sea ice charts indicate that this pathway has a mixed level of ice coverage, ranging from 10-100%. As concentrations decrease once more (24 December), although still passing over water, the trajectory has also increased in height, making it harder to collect any particles produced.

Event 7: (02 January 1993) This event is the hardest to explain, as at no time does the air mass pass over water. On the day of highest concentration the trajectory is also at a particularly high altitude. One possible explanation is that although this event does exhibit a peak in MSA, its concentration is comparatively much lower than the other 7 events (see table 3.6).

3.11.f(i) Conclusion: MSA

In summary, on the day of highest concentration, back trajectories for seven of the eight

events of particularly high aerosol MSA indicate that the air masses, on the day of highest concentration, have previously passed over the ocean 1 -2 days before reaching Halley. Sea ice charts confirm that these areas of ocean, are indeed areas of open water. Trajectories for days when MSA is low in concentration, generally show the air mass to have either travelled entirely over the continent, or ice shelf, or over ocean where the ice coverage is dense (between 90-100%). This work reinforces the theory that MSA and therefore non sea salt sulphate species, have a longer range source, that is not dependant on local meteorological events.

3.11.g Sea Salt Aerosol

Back trajectories for nine events, with high aerosol sea salt concentrations, were calculated and categorised according to whether they passed over land or sea. The results are shown in table 3.7. In general, there appears to be no obvious long range, water source for the high events of aerosol sea salt. Figure 3.32 shows a sea salt back trajectory and figure 3.33, shows the corresponding composite sea ice chart, with 90-100% ice coverage in the area of the trajectory.

Event 1: (18 April 1991) On the day of high sea salt concentration, the air mass passes over the sea five days before reaching Halley. However, weekly sea ice charts for this event show that the sea ice covered the area of the air mass by 90-100%, making contact with open water very unlikely.

Event 2: (16-19 June 1991) The back trajectories for this event indicate that the air mass passed over areas of land and ocean. The sea ice charts for the 17-19 show thick sea ice (90-100%) where the trajectories pass. On the 16 June it is possible that the air mass extends into an ice free zone. However, this is unclear as the ice boundary is estimated for this weekly composite and may be several 10's km out.

Events 3 and 6: (19 July 1991 and 25,26 June 1992) These events clearly show the air mass travelling over the ocean, on the day of high sea salt concentration. The ice charts, however, show no signs of open water in the trajectories pathway for these 2 episodes.

Events 4, 8 and 9: (12 April 1992, 11 August 1992 and 17 November 1992) These three events indicate that the air mass had no contact with open water at any time during the day of highest sea salt concentration.

Events 5 and 7: (19 May 1992 and 28-30 July 1992) Both these episodes of high sea salt have trajectories that pass over land and ocean. In each case, the region of ocean the air mass travels over is covered by 90-100% ice and in some areas, semi-permanent fast ice also. This makes it highly improbable for the air to come in contact with sea spray from open water.

3.11.g(i) Conclusion: Sea Salt

This work demonstrates that the origin for winter sea salt can not be identified by long

range, back trajectory analysis. The air masses on the days of high sea salt concentration were not in contact with open water. This work reinforces the theory put forward earlier in this chapter, that sea salt has a very localised source during the winter, and that open water is not the source. As previously hypothesised, it seems even more likely that local areas of freshly formed ice, housing pools of concentrated brine and frost flowers, are the source for winter sea salt.

3.11.h Overall Back Trajectory Conclusion

For MSA (and nss sulphate), long range air mass origins have been identified using back trajectories. The source of individually high MSA events can be linked to air masses passing over areas of open water. If this is indeed the case, then elevated MSA loadings found in ice cores will not only give information on marine biogenic activity, but also, the extent of open water.

The successful use of back trajectories in identifying this long range source, offers the possibility of predicting high episodes of MSA and nss sulphate from back trajectories that show air masses travelling over open water.

For sea salt, back trajectories have been unsuccessful in establishing a winter aerosol source. This, however, reinforces the theory that the winter sea salt source is a local one.

Table 3.6: Back trajectory predictions for the location of air parcels 1 to 5 days prior to arrival at Halley, run over days when particularly high MSA aerosol concentrations were observed. The trajectory categories and abbreviations are explained in the text.

Event	End Date	Days air mass tracked back					MSA ngm ⁻³	Air masses in same sector after 5 days
		1	2	3	4	5		
1	23 Feb 92	Cc	Cc	Cc	Cc	Cc	19	2
	24 Feb 92	Cc	Cc	Mc	Mc	Mc	39	4
	25 Feb 92	Cc	Cc	Mc	Mo	Mo	105	3
	26 Feb 92	Cc	Cc	Mc	Mo	Mo	95	4
2	28 Feb 92	Mc	Cc	Ci	Ci	Ci	51	3
	29 Feb 92	Cc	Cc	Cc	Cc	Cc	88	3
	01 Mar 92	Cc	Mc	Mc	Cc	Ci	217	4
	02 Mar 92	Cc	Ci	Cc	Cc	Ci	161	3
	03 Mar 92	Cc	Ci	Ci	Ci	Ci	87	3
	04 Mar 92	Cc	Cc	Cc	Cc	Mc	31	3
3	06 Mar 92	Cc	Cc	Ci	Ci	Ci	17	4
	07 Mar 92	Cc	Mc	Ci	Ci	Ci	140	4
	08 Mar 92	Mc	Cc	Ci	Ci	Ci	—	4
	09 Mar 92	Mo	Mc	Cc	Cc	Ci	51	3
4	10 Mar 92	Mc	Mc	Mc	Ci	Ci	19	1
	11 Mar 92	Mc	Cc	Cc	Cc	Ci	116	4
	12 Mar 92	Mc	Cc	Ci	Ci	Ci	41	4
5	10 Dec 92	Co	Cc	Cc	Co	Mo	—	3
	11 Dec 92	Co	Mo	Mc	Mo	Mo	15	2
	12 Dec 92	Cc	Mc	Mo	Mc	Mc	54	2
	13 Dec 92	Cc	Ci	Cc	Ci	Ci	3	3
6	21 Dec 92	Cc	Ci	Ci	Cc	Ci	4	4
	22 Dec 92	Cc	Ci	Ci	Ci	Ci	23	4
	23 Dec 92	Mc	Mo	Mo	Mo	Mo	120	3
	24 Dec 92	Cc	Mc	Mo	Mc	Mo	71	1
7	01 Jan 93	Cc	Cc	Cc	Cc	Cc	8	3
	02 Jan 93	Cc	Cc	Ci	Cc	Cc	159	4
	03 Jan 93	Cc	Ci	Ci	Ci	Ci	13	4
	04 Jan 93	Cc	Cc	Cc	Cc	Ci	53	4
8	05 Jan 93	Cc	Cc	Cc	Cc	Cc	36	4
	06 Jan 93	Mc	Mo	Mc	Cc	Ci	105	4
	07 Jan 93	Ci	Cc	Ci	Ci	Ci	59	4
	08 Jan 93	Cc	Ci	Cc	Cc	Cc	23	4
	09 Jan 93	Cc	Ci	Ci	Cc	Cc	6	4

Table 3.7: Back trajectory predictions for the location of air parcels 1 to 5 days prior to arrival at Halley, run over days when particularly high sea salt aerosol concentrations were observed. The trajectory categories and abbreviations are explained in the text.

Event	End Date	Days air mass tracked back					Sea Salt ngm ⁻³	Air masses in same sector after 5 days
		1	2	3	4	5		
1	16 Apr 91	Cc	Cc	Mc	Mc	Mc	13	1
	17 Apr 91	Ci	Ci	Ci	Ci	Ci	24	4
	18 Apr 91	Ci	Ci	Ci	Cc	Mc	1209	1
	19 Apr 91	Cc	Cc	Cc	Mo	Mo	883	3
	20 Apr 91	Cc	Cc	Mc	Mo	Mo	394	4
	21 Apr 91	Ci	Ci	Ci	Ci	Ci	148	3
2	14 June 91	Cc	Mo	Mo	Mo	Mo	95	3
	15 June 91	Mo	Mo	Mc	Cc	Cc	----	0
	16 June 91	Cc	Mo	Mo	Mc	Mc	1456	4
	17 June 91	Cc	Ci	Mo	Mo	Mc	1376	0
	18 June 91	Cc	Ci	Mc	Mo	Mo	1142	3
	19 June 91	Cc	Mc	Mo	Mc	Mc	1659	2
	20 June 91	Cc	Cc	Mc	Mc	Cc	652	4
	21 June 91	Mc	Cc	Cc	Cc	Cc	97	3
3	18 July 91	Cc	Mc	Mo	Mo	Mo	62	3
	19 July 91	Mc	Mc	Mc	Mo	Mo	2264	4
	20 July 91	Mc	Mc	Cc	Ci	Cc	686	1
	21 July 91	Cc	Mc	Cc	Cc	Ci	59	1
4	11 Apr 92	Cc	Ci	Cc	Mc	Mc	20	0
	12 Apr 92	Ci	Ci	Ci	Cc	Cc	528	2
	13 Apr 92	Ci	Ci	Ci	Ci	Ci	412	3
	14 Apr 92	Ci	Ci	Ci	Ci	Ci	186	3
	15 Apr 92	Ci	Ci	Ci	Ci	Ci	4	4

Event	End Date	Days air mass tracked back					Sea Salt ngm ⁻³	Air masses in same sector after 5 days
		1	2	3	4	5		
5	17 May 92	Mc	Cc	Ci	Ci	Ci	36	3
	18 May 92	Mc	Cc	Ci	Ci	Ci	54	4
	19 May 92	Cc	Mc	Mc	Mc	Mo	292	0
	20 May 92	Cc	Ci	Cc	Mc	Mc	218	1
	21 May 92	Mc	Cc	Ci	Ci	Ci	38	3
6	23 June 92	Mc	Mo	Mo	Mo	Mo	81	0
	24 June 92	Mo	Mo	Mo	Cc	Cc	----	2
	25 June 92	Mc	Mo	Mo	Mc	Mo	1331	3
	26 June 92	Mc	Mc	Mo	Mo	Mc	1264	2
	27 June 92	Cc	Ci	Mo	Mo	Mo	195	1
	28 June 92	Cc	Ci	Ci	Cc	Mc	47	2
7	26 July 92	Cc	Ci	Ci	Ci	Ci	127	4
	27 July 92	Cc	Mc	Mc	Cc	Ci	499	4
	28 July 92	Cc	Mc	Mc	Cc	Ci	900	2
	29 July 92	Ci	Ci	Ci	Cc	Mc	1088	3
	30 July 92	Cc	Cc	Mc	Mc	Mc	1208	3
	31 July 92	Cc	Cc	Mc	Mc	Mc	386	3
	01 Aug 92	Cc	Cc	Mc	Mc	Mc	152	2
8	09 Aug 92	Cc	Cc	Mc	Mc	Mc	----	4
	10 Aug 92	Ci	Ci	Ci	Ci	Ci	552	3
	11 Aug 92	Cc	Ci	Ci	Ci	Ci	2181	4
	12 Aug 92	Ci	Ci	Ci	Ci	Ci	205	3
9	15 Nov 92	Mo	Mo	Mo	Mo	Mo	54	4
	16 Nov 92	Mo	Mc	Mo	Mo	Mo	85	2
	17 Nov 92	Cc	Ci	Ci	Cc	Cc	710	4
	18 Nov 92	Cc	Ci	Ci	Cc	Cc	438	4
	19 Nov 92	Cc	Cc	Ci	Ci	Ci	13	4

Figure 3.1: Daily, raw data for aerosol sea salt components measured at Halley.

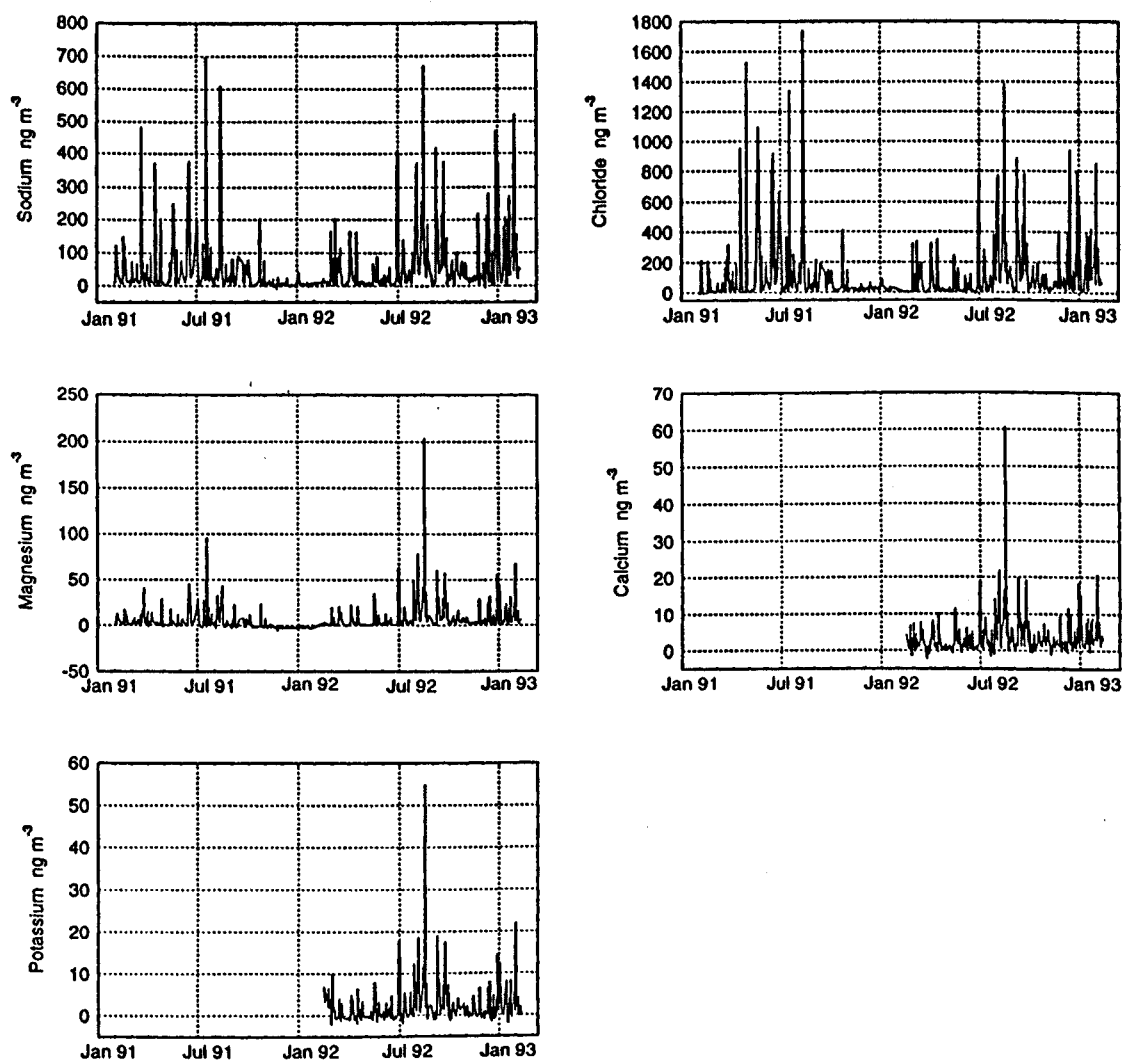


Figure 3.2: Monthly averages for aerosol sea salt components measured at Halley.

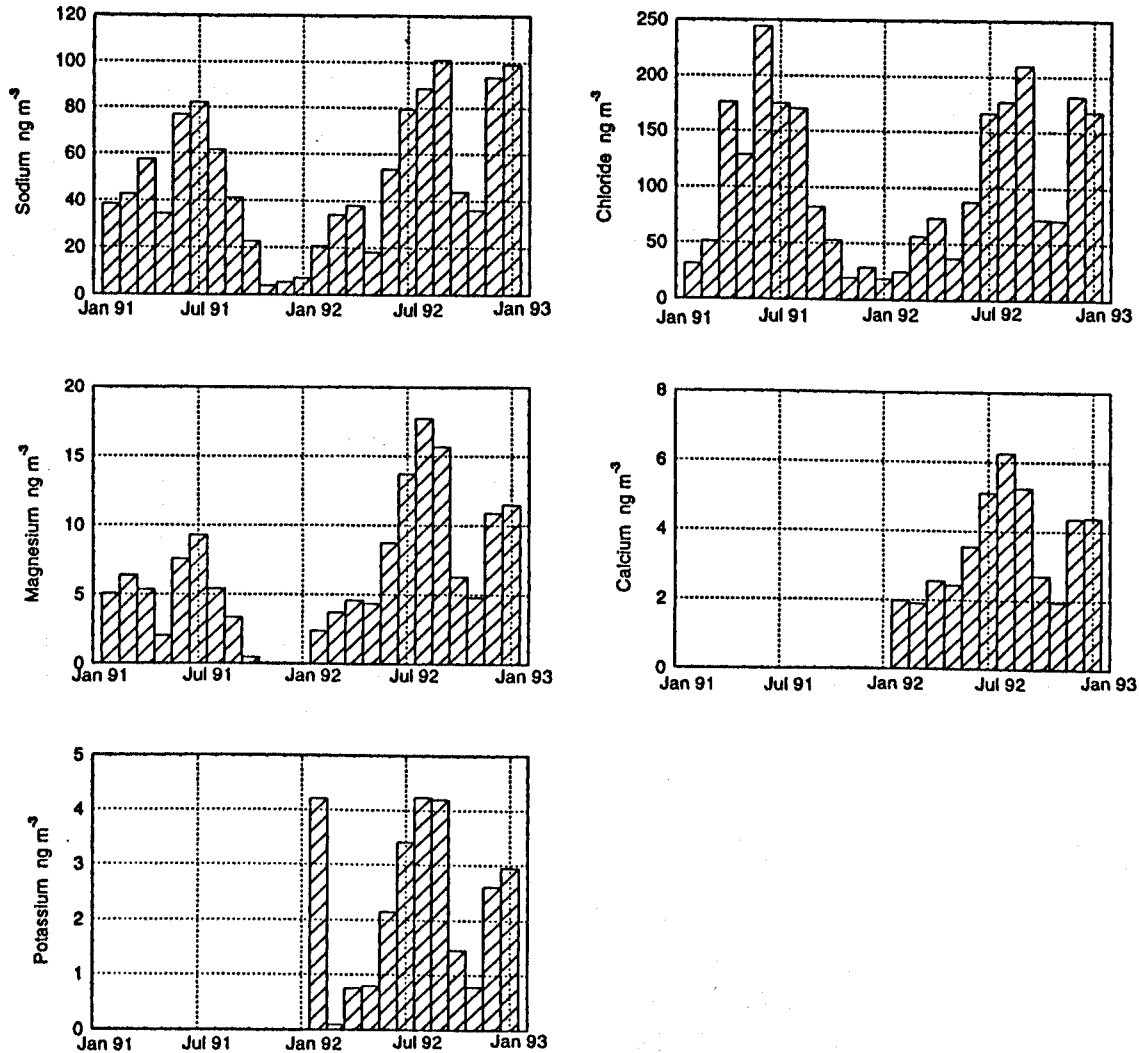


Figure 3.3a: Daily, raw data for aerosol sea salt, (calculated from sodium data) measured at Halley.

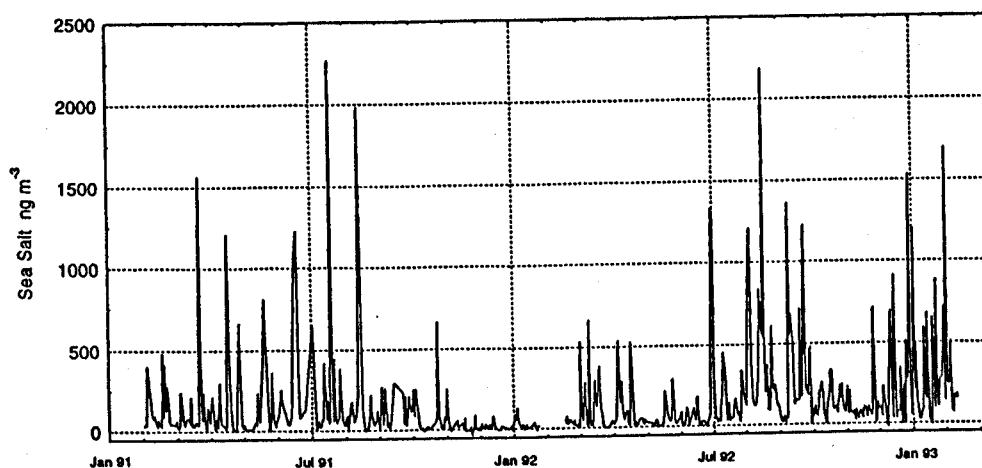


Figure 3.3b: Monthly averages for aerosol sea salt measured at Halley.

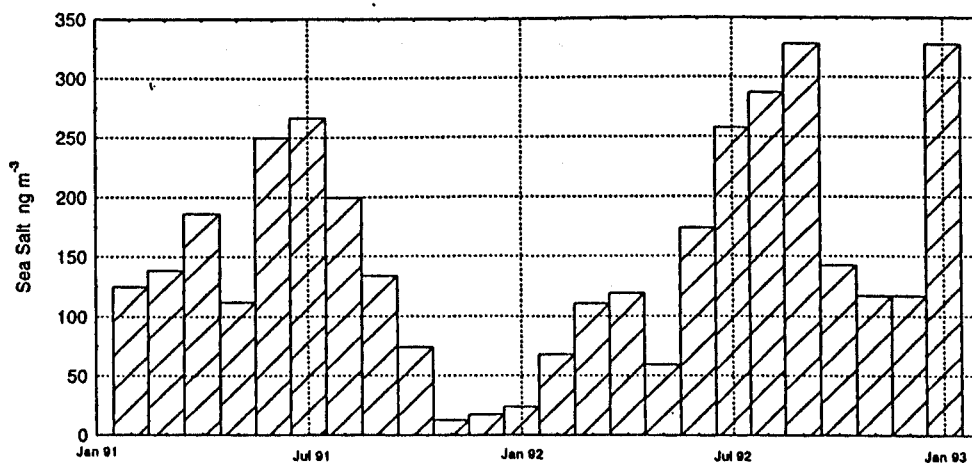


Figure 3.4: Location of other sea salt measuring Antarctic bases.

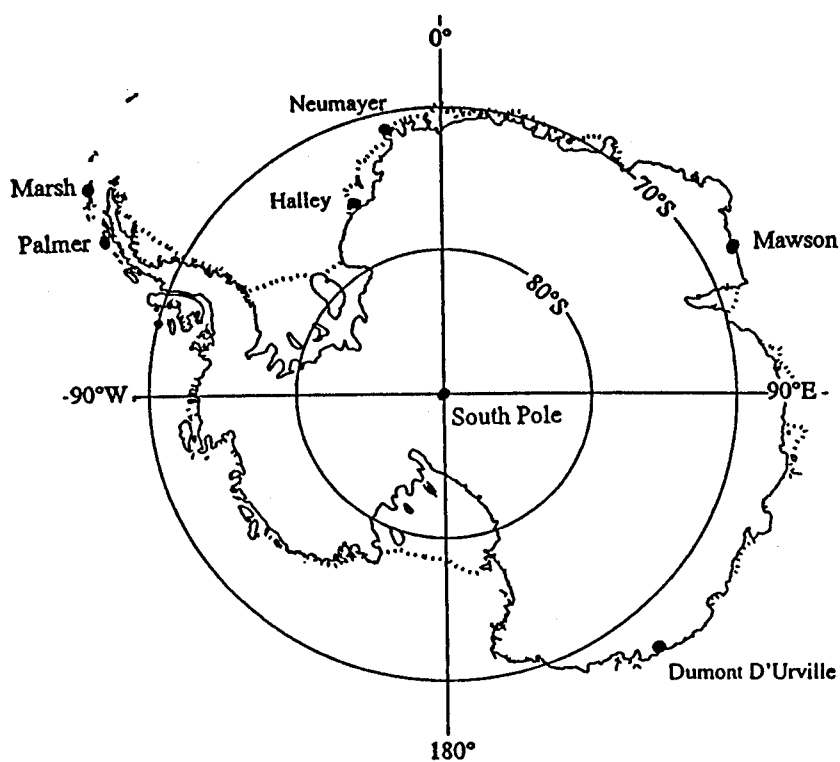


Figure 3.5: Particle behaviour at sampling inlets under non-isokinetic conditions. Larger particles are excluded when the inlet air velocity is greater than the main air stream. Taken from Murphy, [1984].

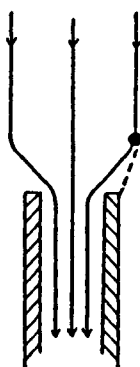


Figure 3.6a: High episodes of aerosol sea salt (solid line and squares) at Halley during 1991, plotted with associated wind speed and direction (solid line). The date on the x-axis begins at 00:01am of that day and the samples are plotted at midday, approximately when they were originally removed. Westerly winds are plotted as negative and easterly as positive. For the purpose of these two plots easterly winds are taken as 0° - 180° and westerlies as 180° - 360° .

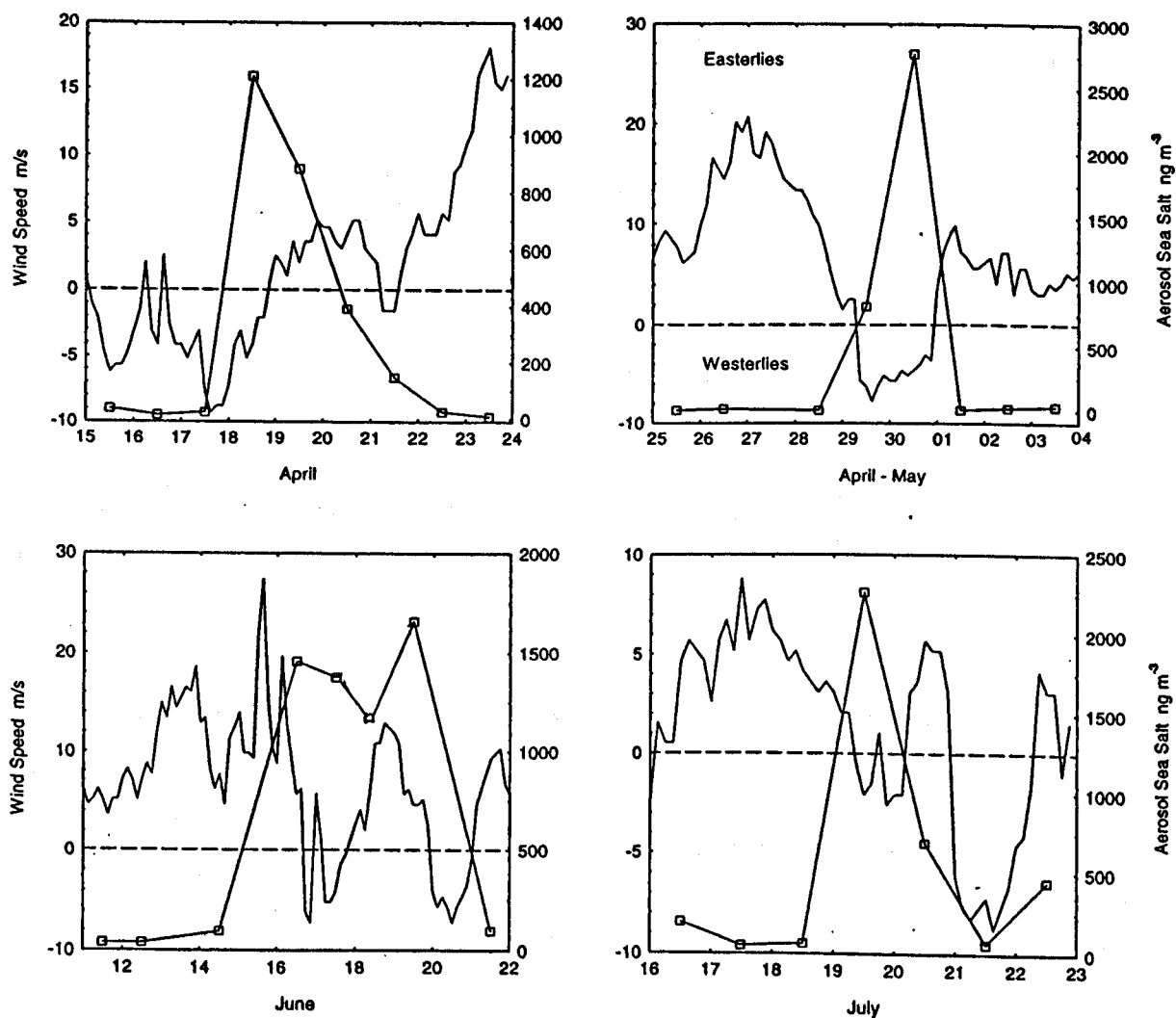


Figure 3.6b: High episodes of aerosol sea salt (solid line and squares) at Halley during 1992, plotted with associated wind speed and direction (solid line). The date on the x-axis begins at 00:01am of that day and the samples are plotted at midday, approximately when they were originally removed. Westerly winds are plotted as negative and easterly as positive. For the purpose of these two plots easterly winds are taken as 0° - 180° and westerlies as 180° - 360° .

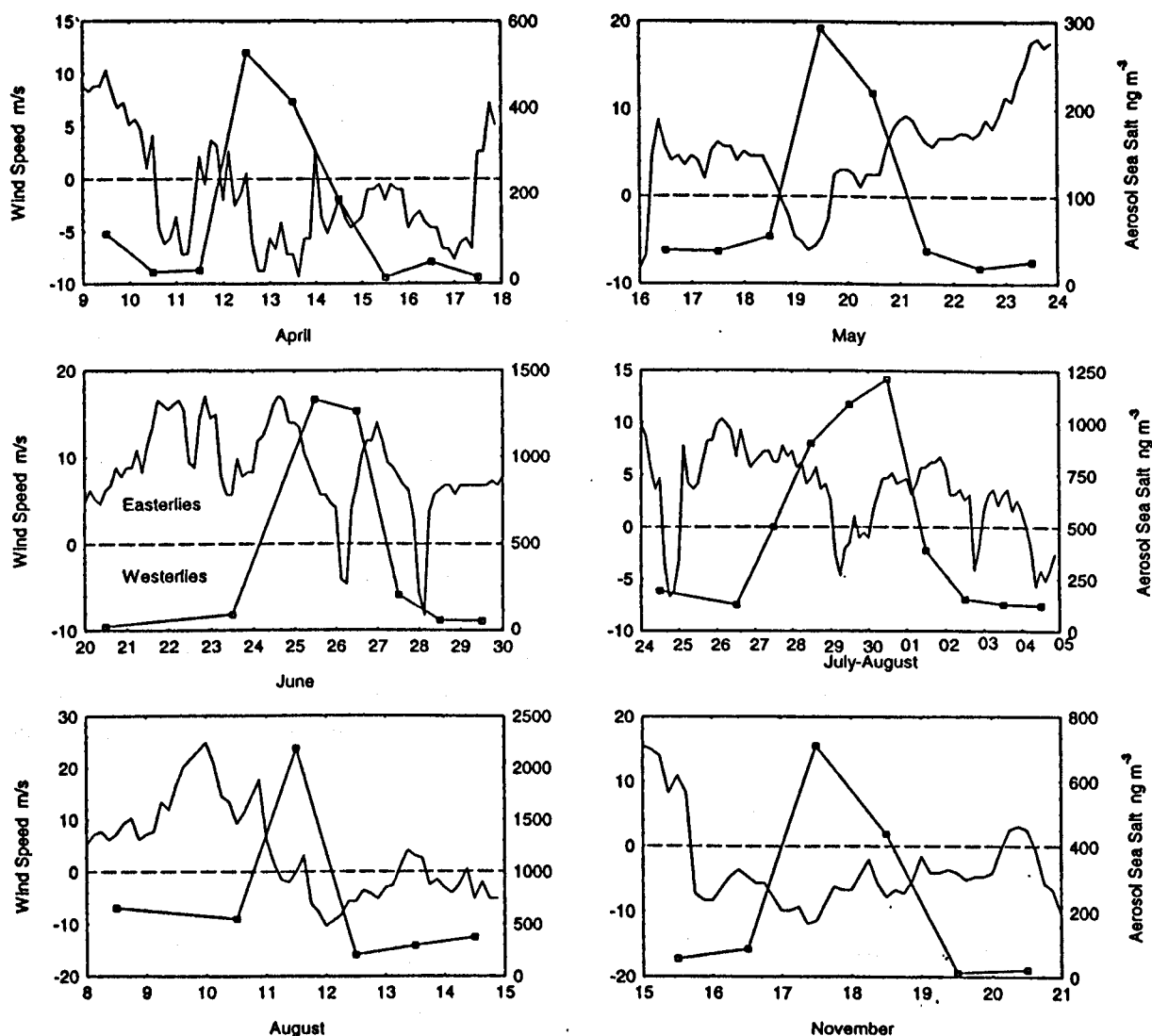


Figure 3.7a: Close up of frost flowers.

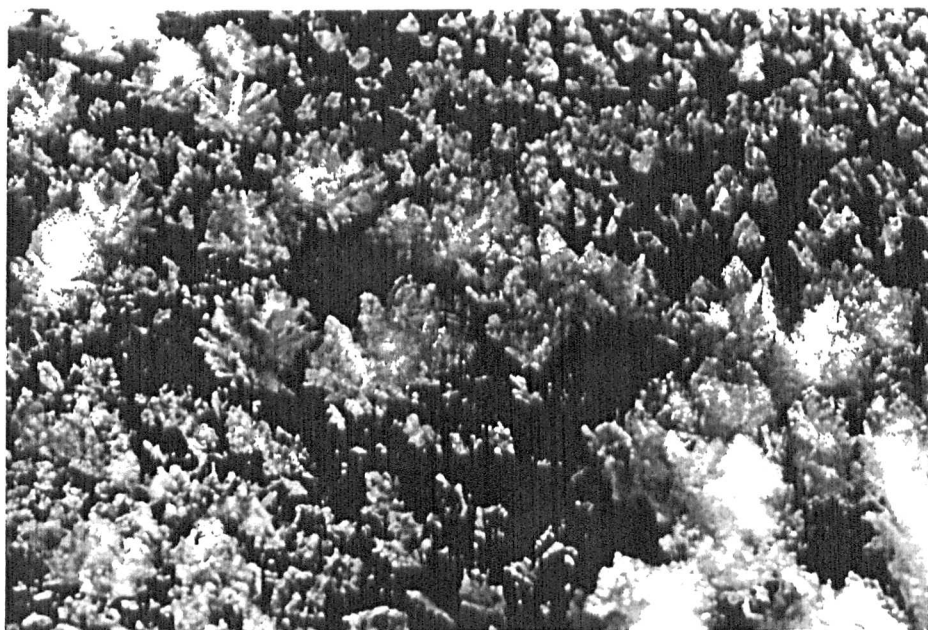


Figure 3.7b: An expanse of newly formed ice, covered by frost flowers, located 15 km to the west of Halley.

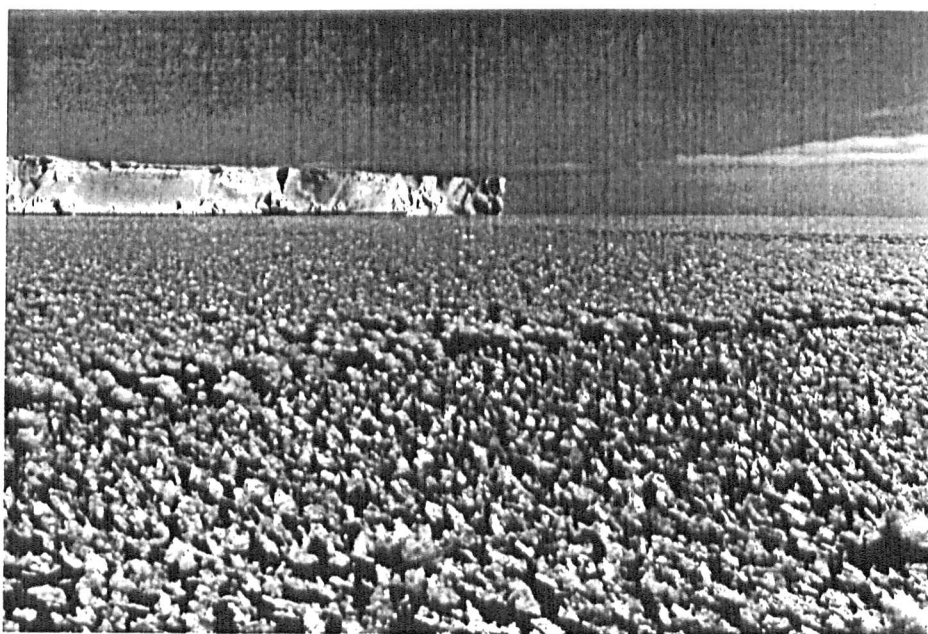


Figure 3.8: Scatter plot for non sea salt sulphate (calculate using sodium data and assuming $[\text{SO}_4^{2-}]/[\text{Na}^+]$ to be in bulk sea water ratio) versus sodium for the complete Halley aerosol record. Winter values shown as filled squares and summer points as open circles. The regression line is calculated using the winter values only, $y = -0.143x + 16.2$.

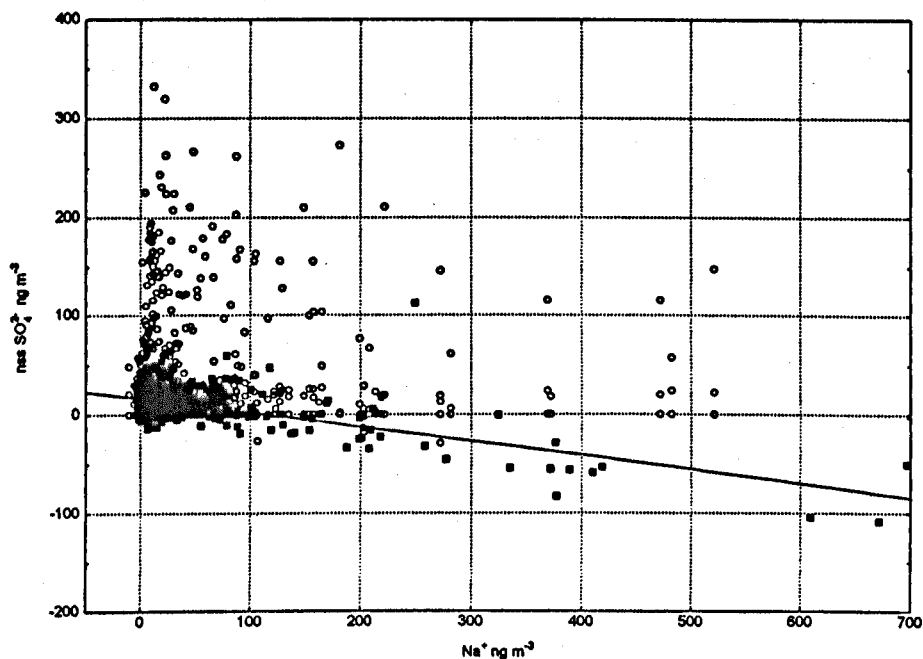


Figure 3.9: Scatter plots of the major cations versus sodium, in ng m^{-3} , with a best fitted line superimposed. These simple linear regressions can be described as magnesium $y = 0.134x - 0.373$, potassium $y = 0.038x - 0.172$ and calcium $y = 0.043x + 0.873$.

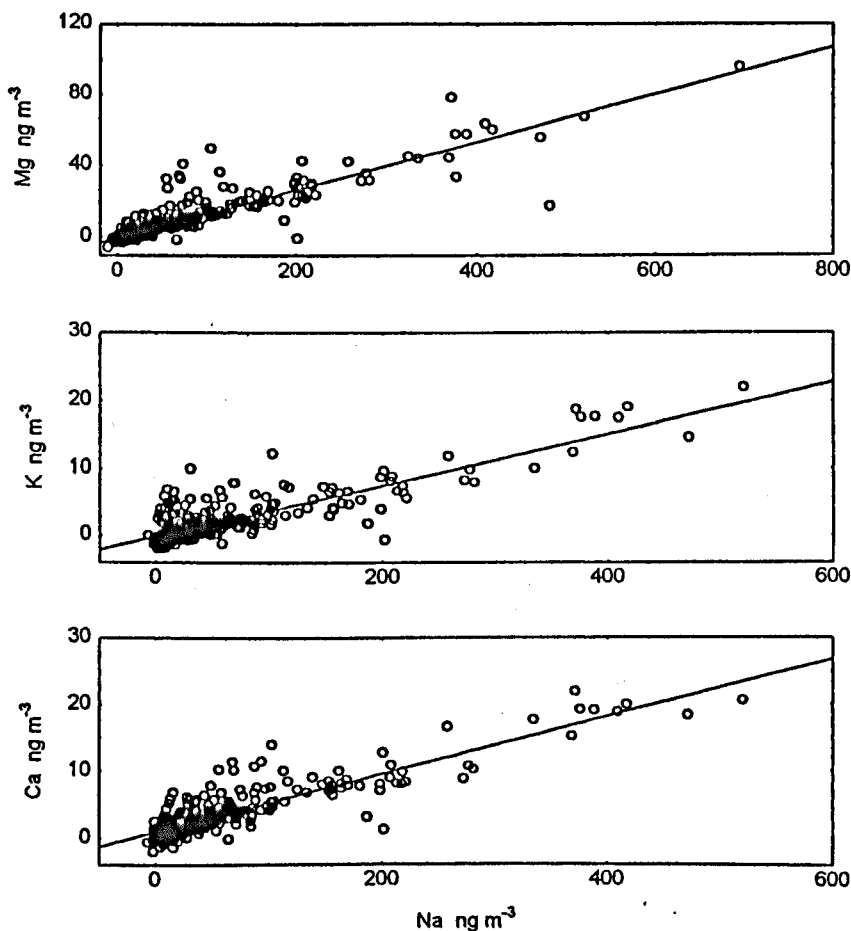


Figure 3.10: Sulphate to sodium ratios (circles) on days of high aerosol sea salt, plotted with the bulk sea water ratio (solid line) for sulphate to sodium.

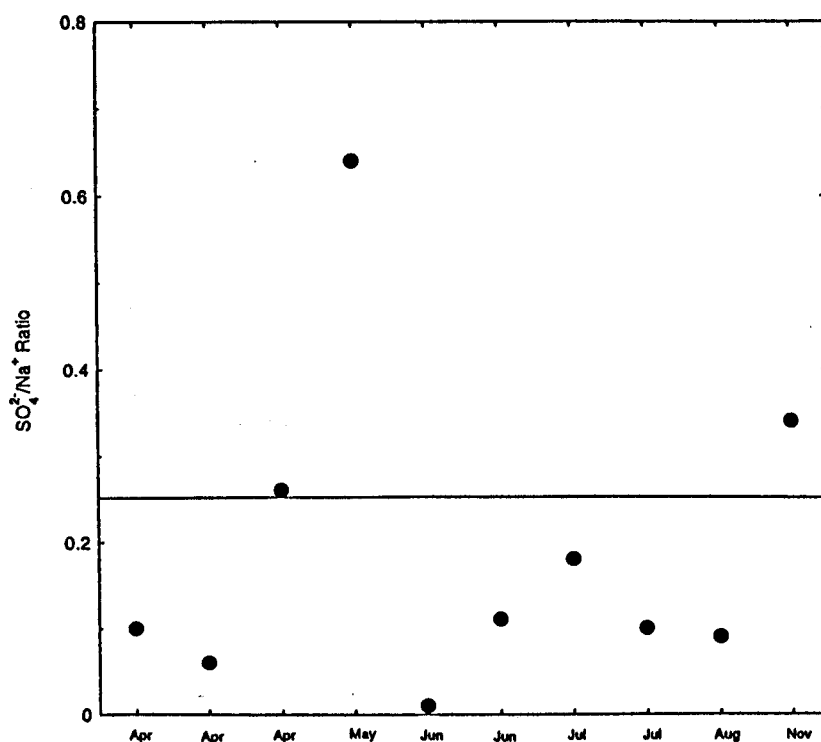


Figure 3.11: Representative high episodes of aerosol sea salt (solid line and squares) at Halley during 1991 and 1992, plotted with associated daily surface temperature (solid line). The date on the x-axis begins at 00:01am of that day and the samples are plotted at midday, approximately when they were originally removed.

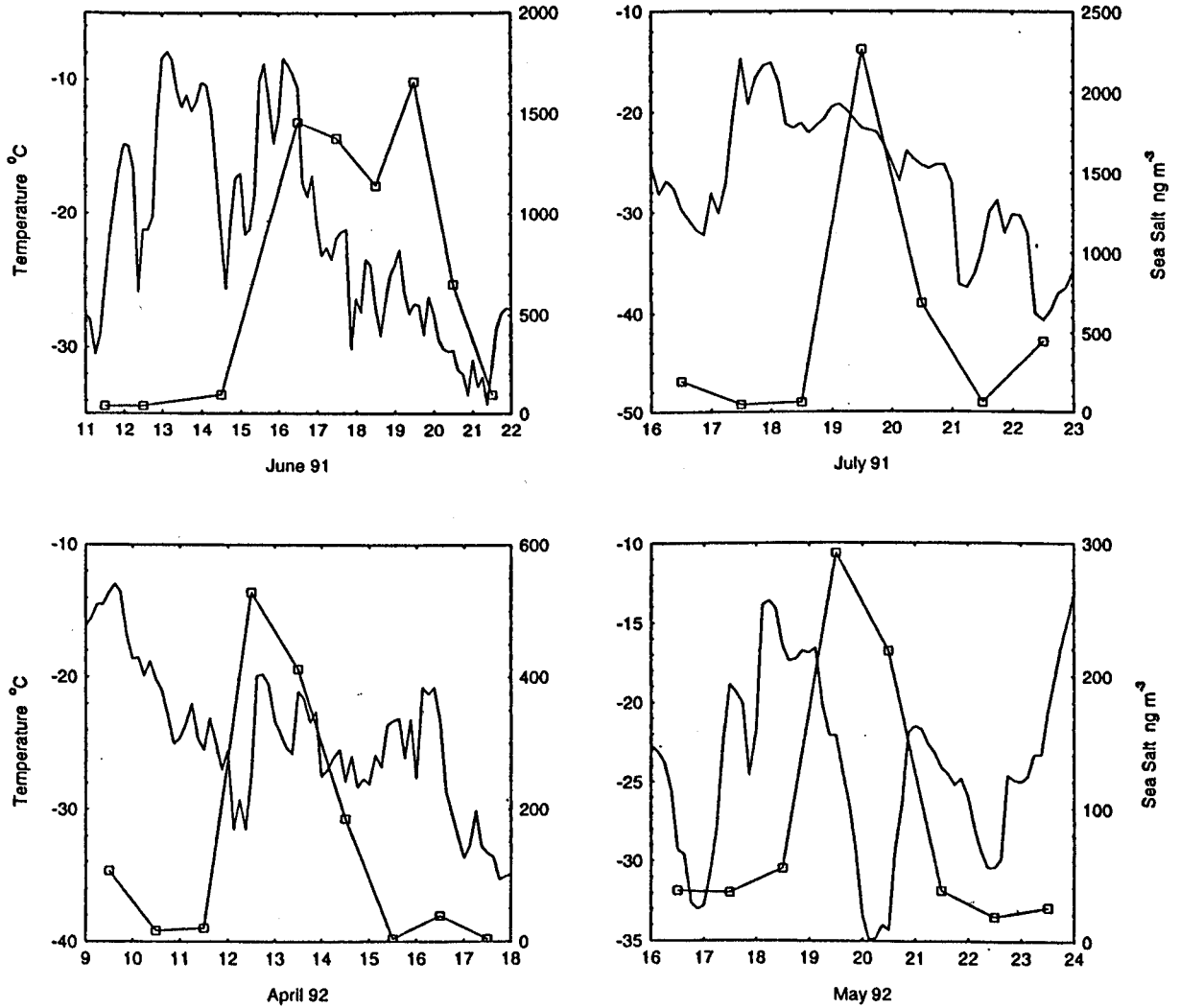


Figure 3.12: Possible sources of sulphate present in Antarctica
 NB: Adapted from Legrand, [1995].

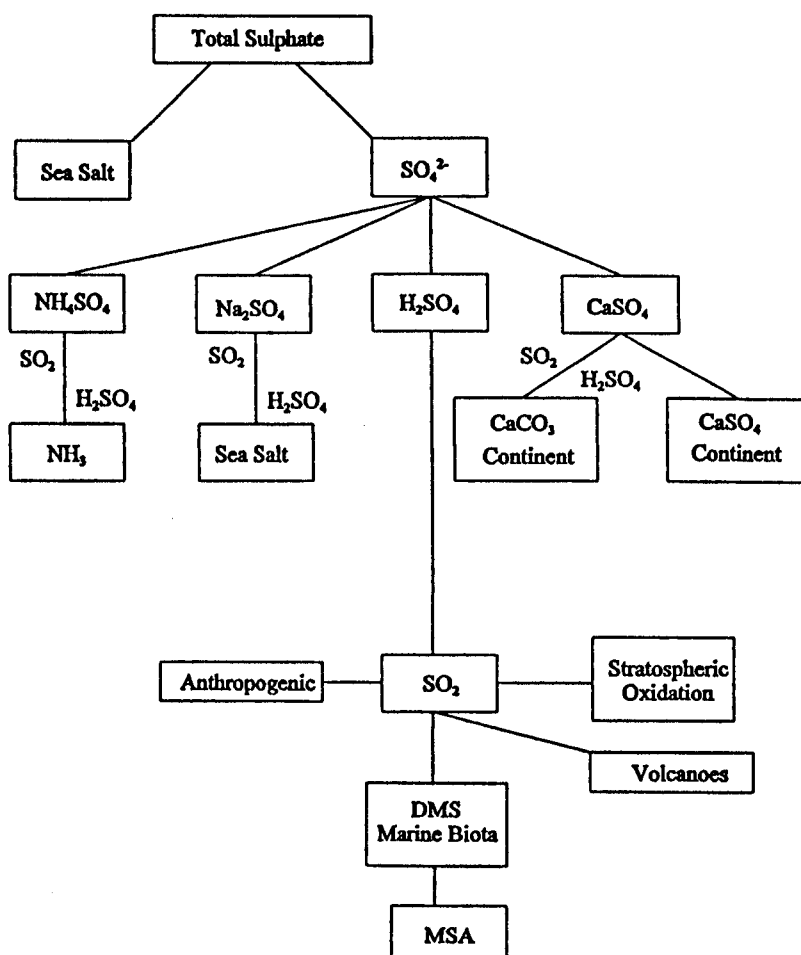


Figure 3.13: Flow diagram highlighting the key stages in biogenic sulphur production.

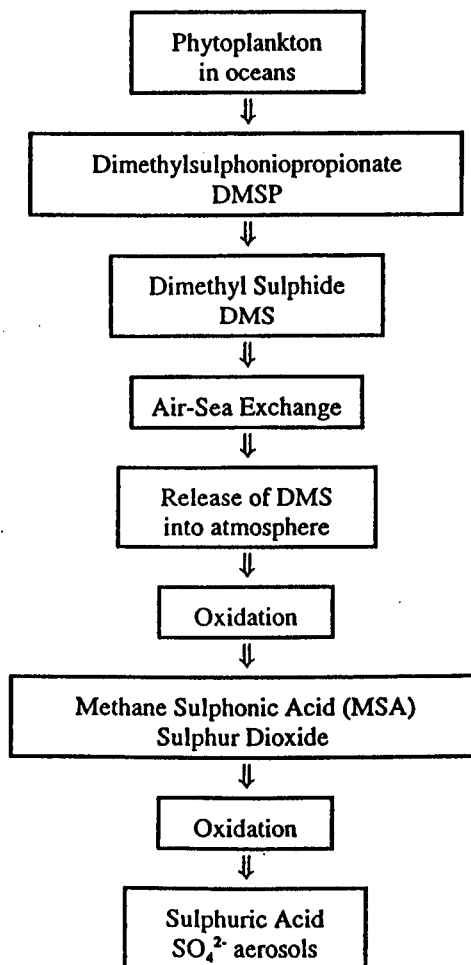


Figure 3.14: Black carbon (BC) data (solid lines, left axis) and daily aerosol sulphate concentrations (dashed line, right axis) for two periods in 1992. The top plot is from autumn 1992, when non sea salt sulphate is elevated, and the lower plot is from the winter, when nss sulphate concentrations are at their lowest [Taken from Wolff and Cachier, in press].

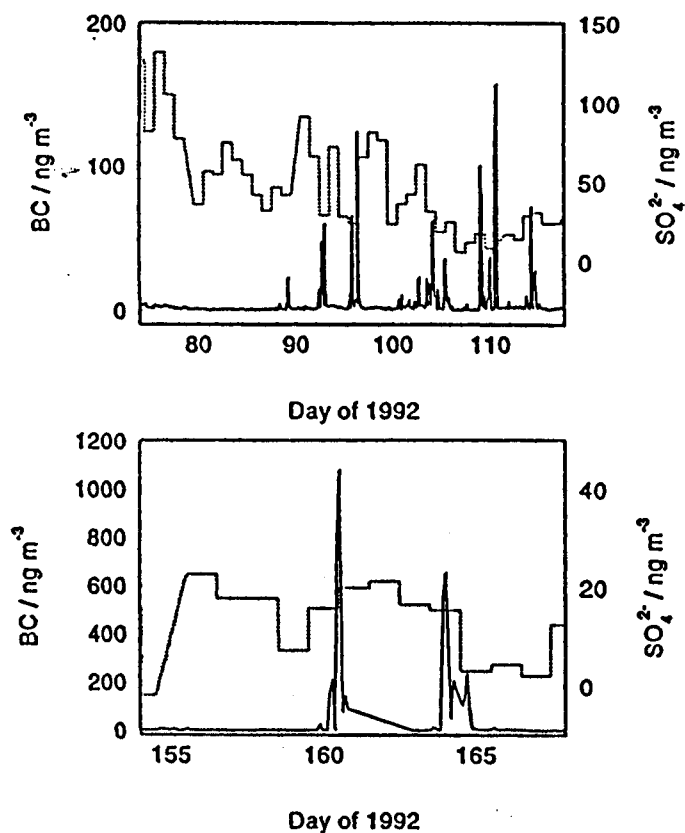


Figure 3.15: *Corrected nss sulphate (upper plot) and nss sulphate calculated using 0.252 as BSW ratio (lower plot).*

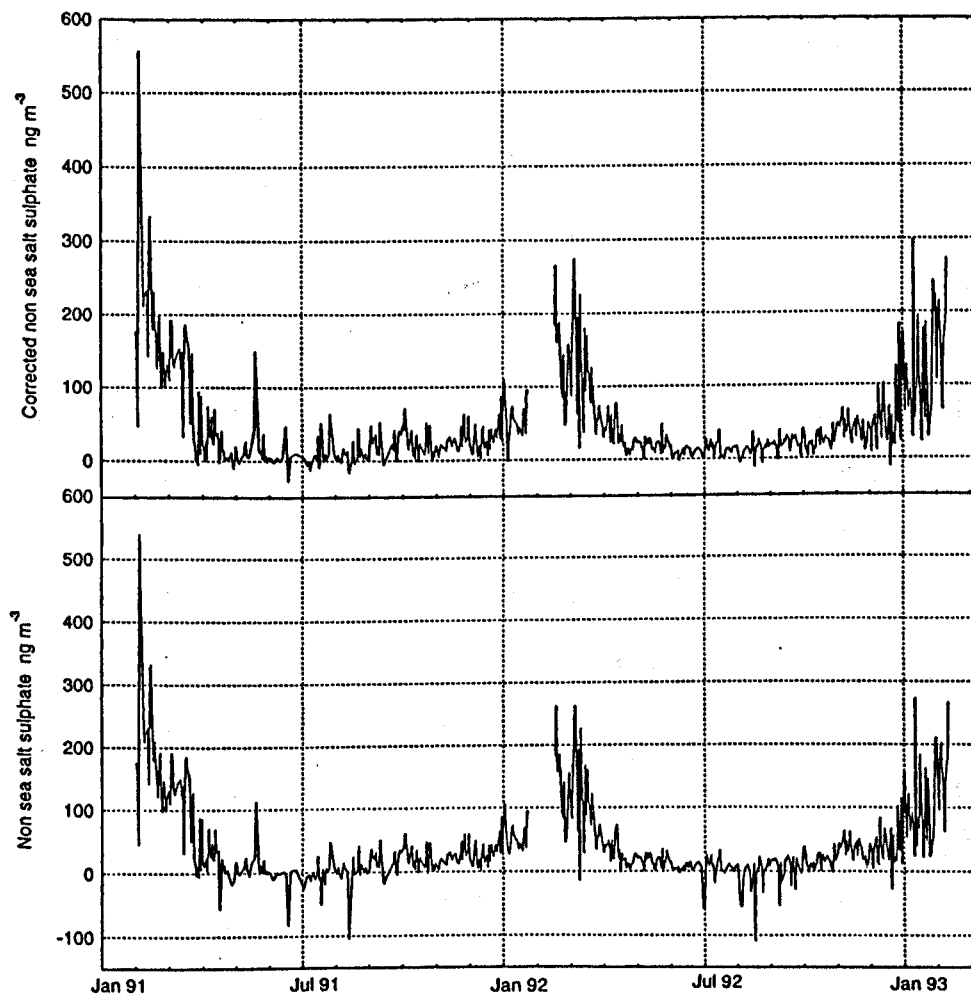


Figure 3.16: Daily, raw data for aerosol corrected non sea salt sulphate and methane sulphonic acid at Halley.

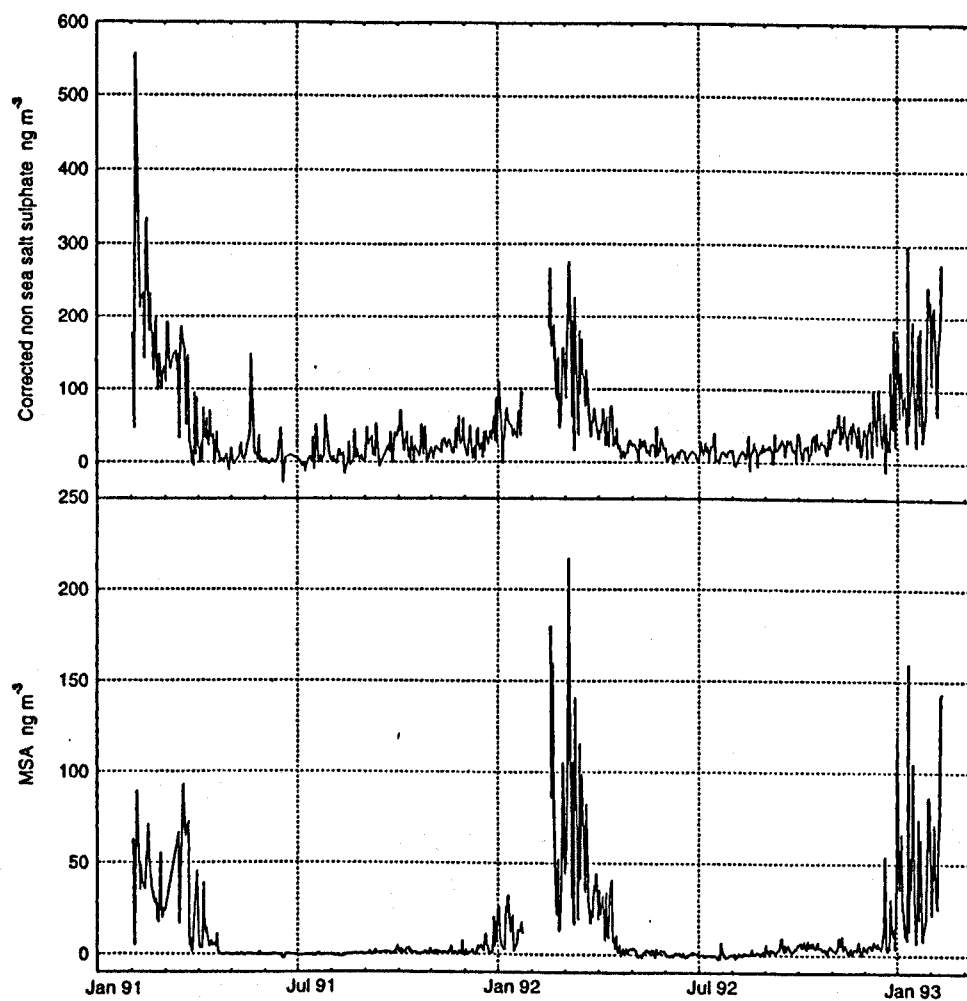


Figure 3.17: Monthly averages for aerosol nss sulphate and MSA at Halley.

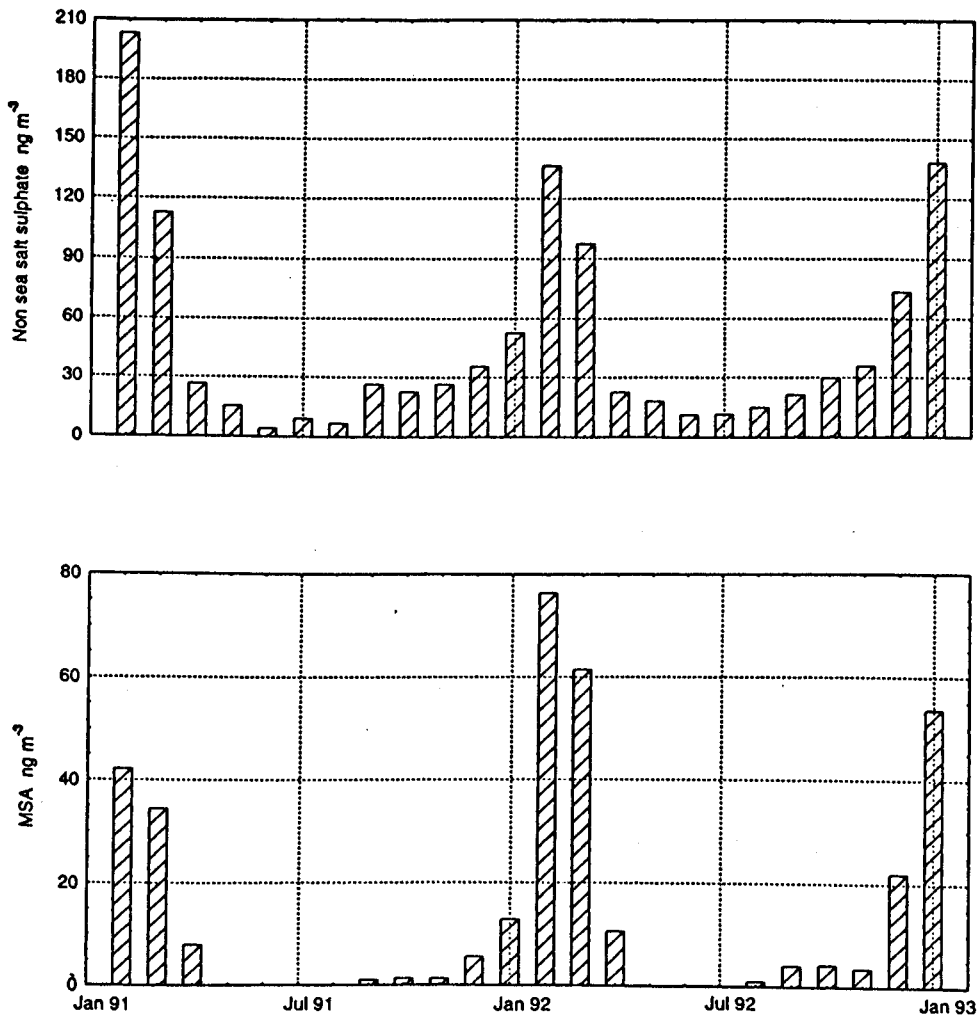


Figure 3.18a: Atmospheric DMS seasonal cycle from Cape Grim, Tasmania. Taken from Ayers et al., [1991].

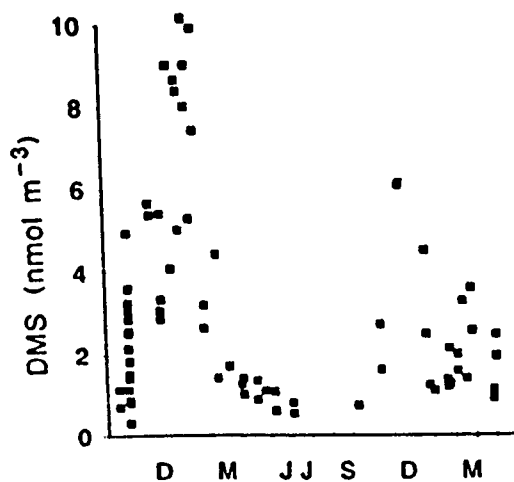


Figure 3.18b: Atmospheric DMS seasonal cycle from Neumayer station, Antarctica. Taken from Minikin et al., [submitted].

DMS raw data points (dots) and smoothed average (solid line).

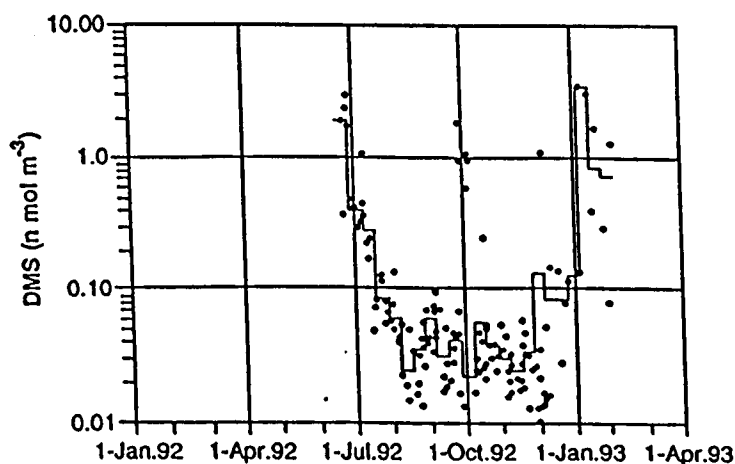


Figure 3.19: Aerosol non sea salt sulphate seasonal cycles at four Antarctic stations, plotted as 10 day averages. Monthly mean chlorophyll concentrations from latitudes higher than 50°S, higher than 60°S and between 50 and 60°S. Taken from Minikin et al., [submitted].

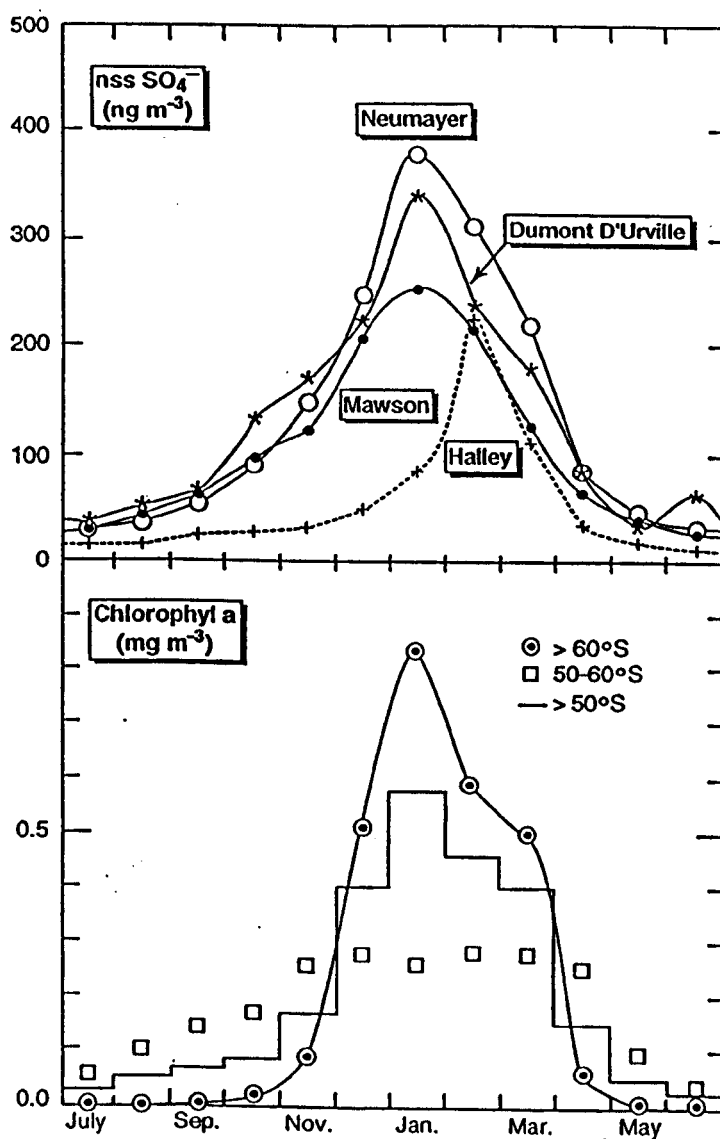


Figure 3.20: Aerosol non sea salt sulphate and MSA concentrations, plotted with corresponding local temperature.

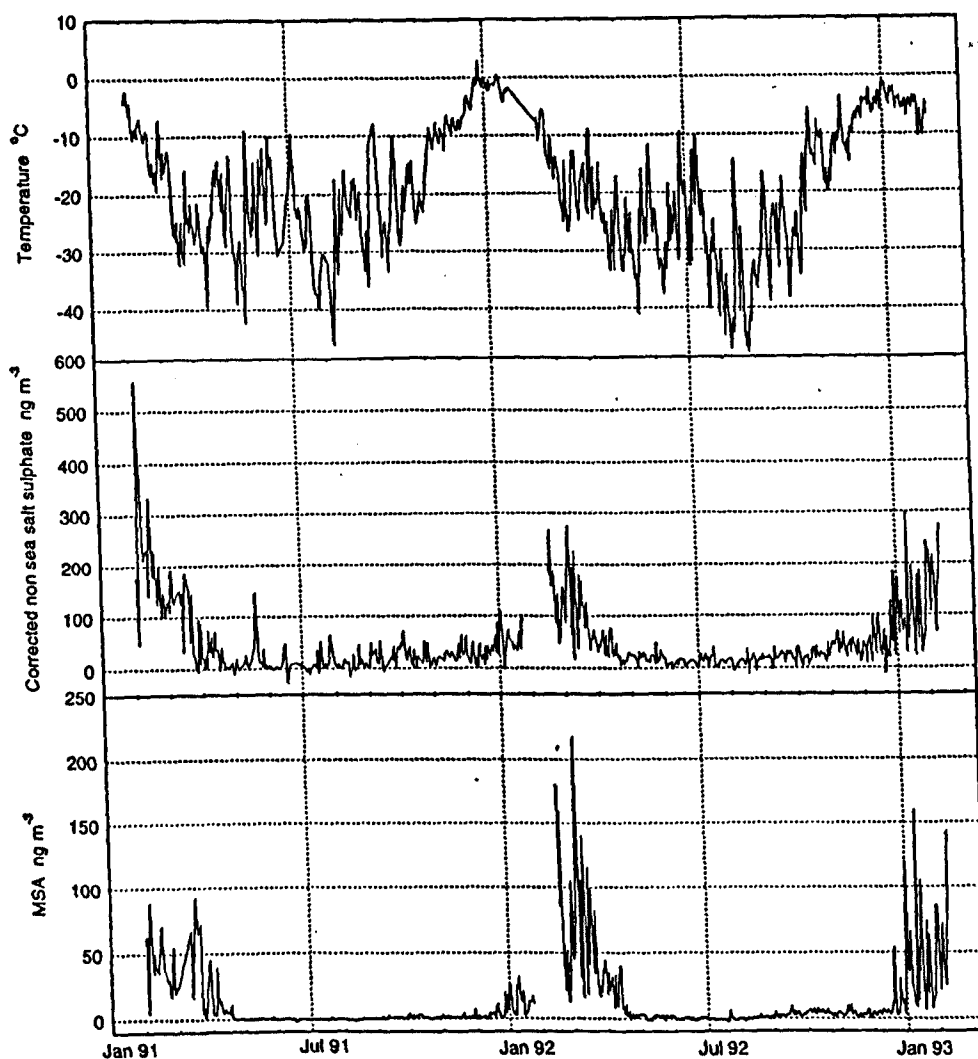


Figure 3.21: Seasonal time series of aerosol MSA/nss sulphate at Halley. Both corrected (BSW ratio of 0.107, shown with solid line and crosses) and traditional (BSW ratio of 0.252, dashed line and squares) nss sulphate concentrations have been used.

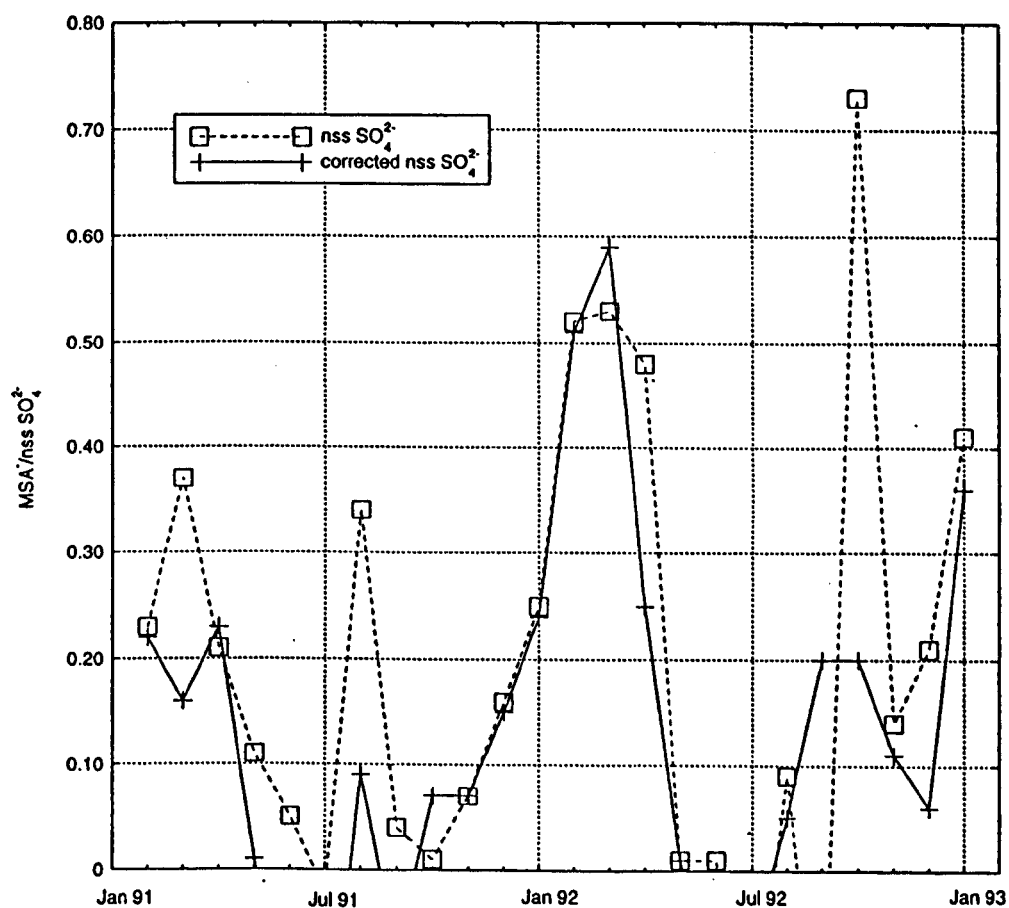


Figure 3.22: Scatter plot of nss sulphate versus MSA aerosol concentrations at Halley., with a least squares regression superimposed. Winter values are plotted on the bottom graph, ($y=2.37x+12.8$) and summer values plotted above, ($y=1.54x+33.6$).

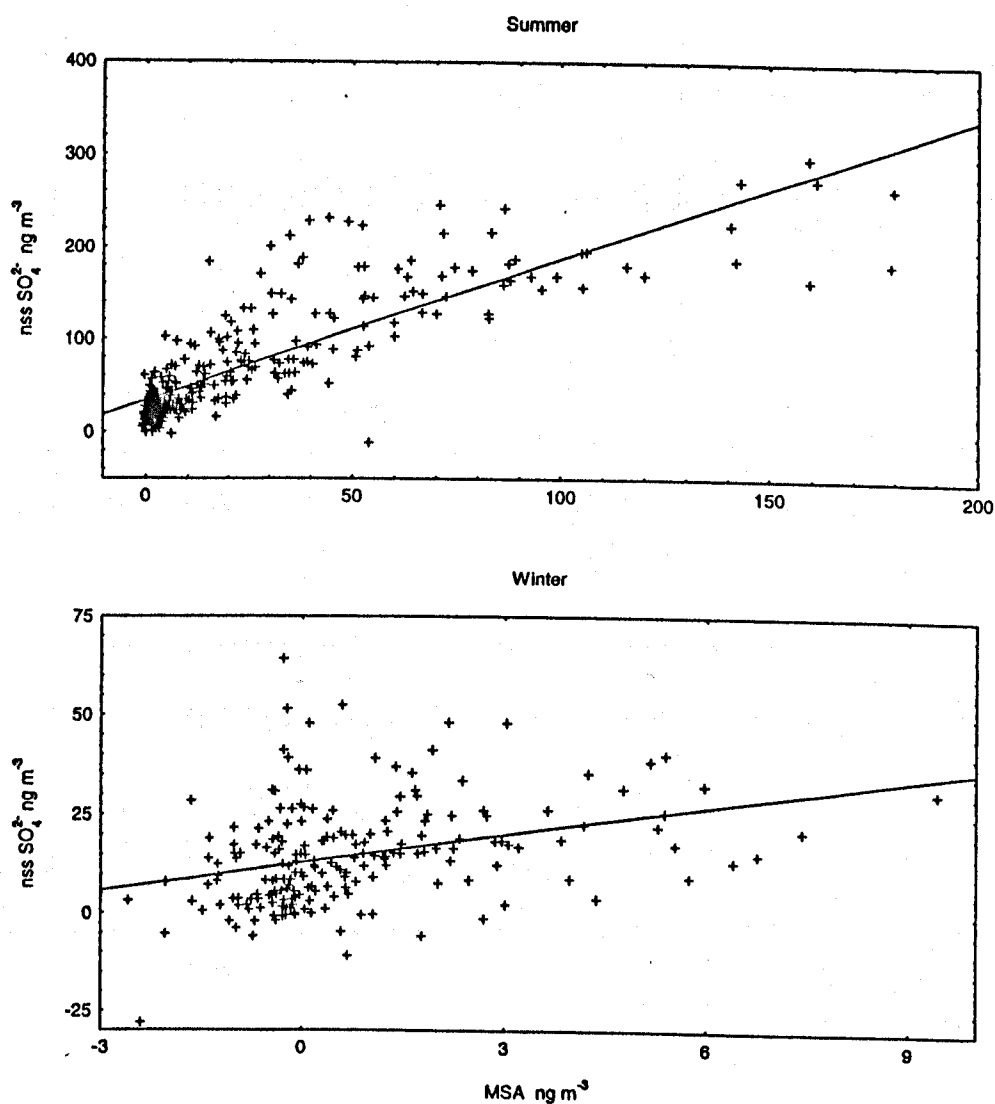


Figure 3.23: High episodes of aerosol methane sulphonc acid (solid line and squares) at Halley, plotted with associated wind speed and direction (solid line). The date on the x-axis begins at 00:01am of that day and the samples are plotted at midday, approximately when they were originally removed. Westerly winds are plotted as negative and easterly as positive. For the purpose of these two plots easterly winds are taken as 0° - 180° and westerlies as 180° - 360° .

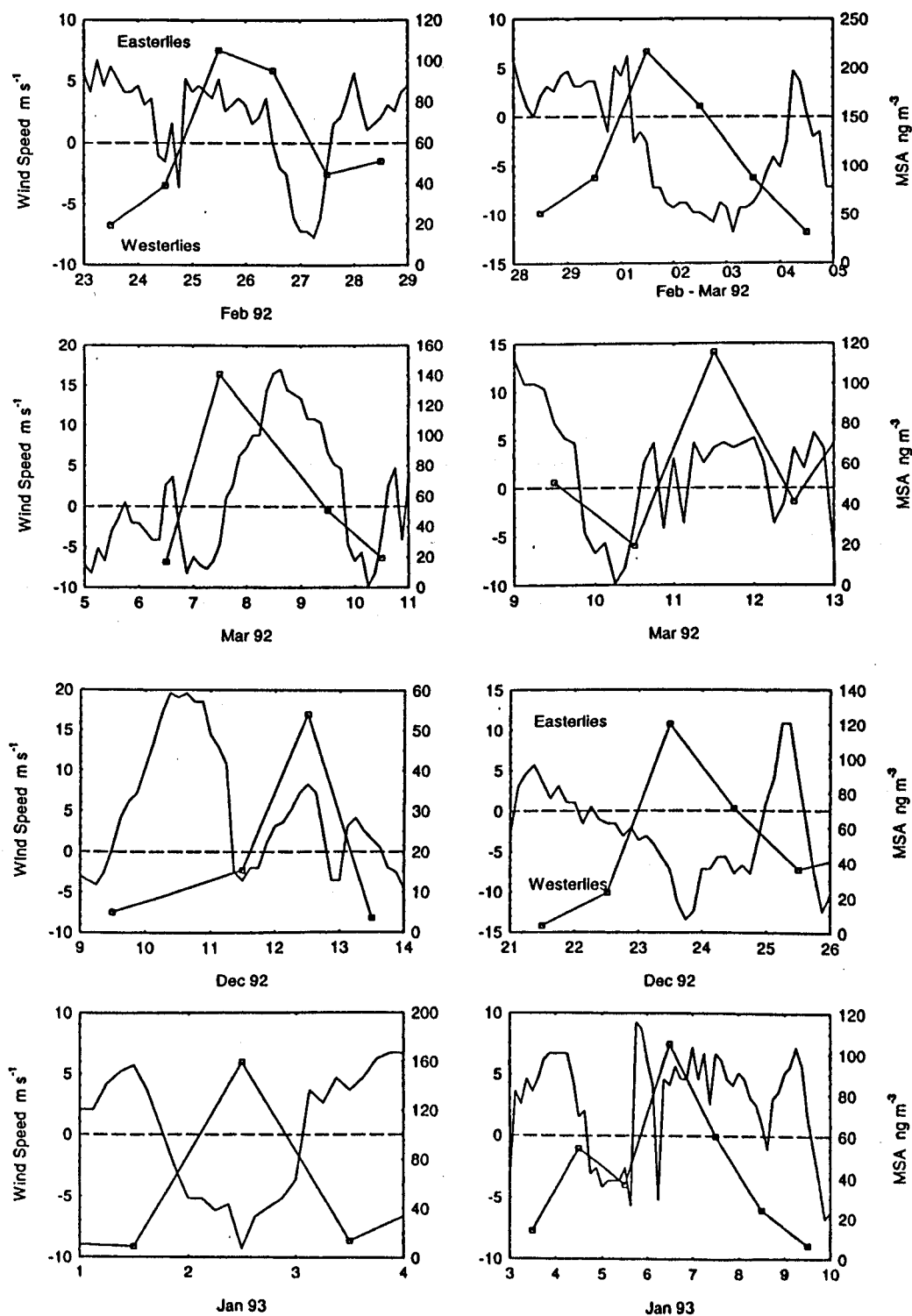


Figure 3.24: Average MSA (bottom solid line and crosses) and non sea salt sulphate concentrations (top solid line and squares) during particular wind directions (bar graph). Wind direction is plotted against frequency of days.

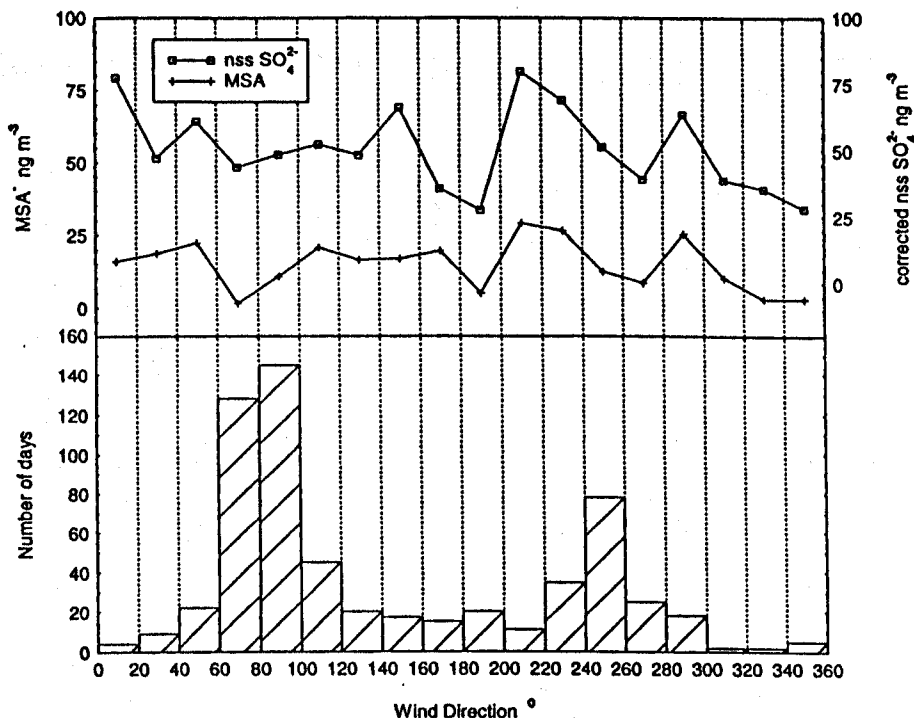


Figure 3.25: Average summer MSA (bottom solid line and crosses) and summer non sea salt sulphate concentrations (top solid line and squares) during particular summer wind directions (bar graph). Wind direction is plotted against frequency of days.

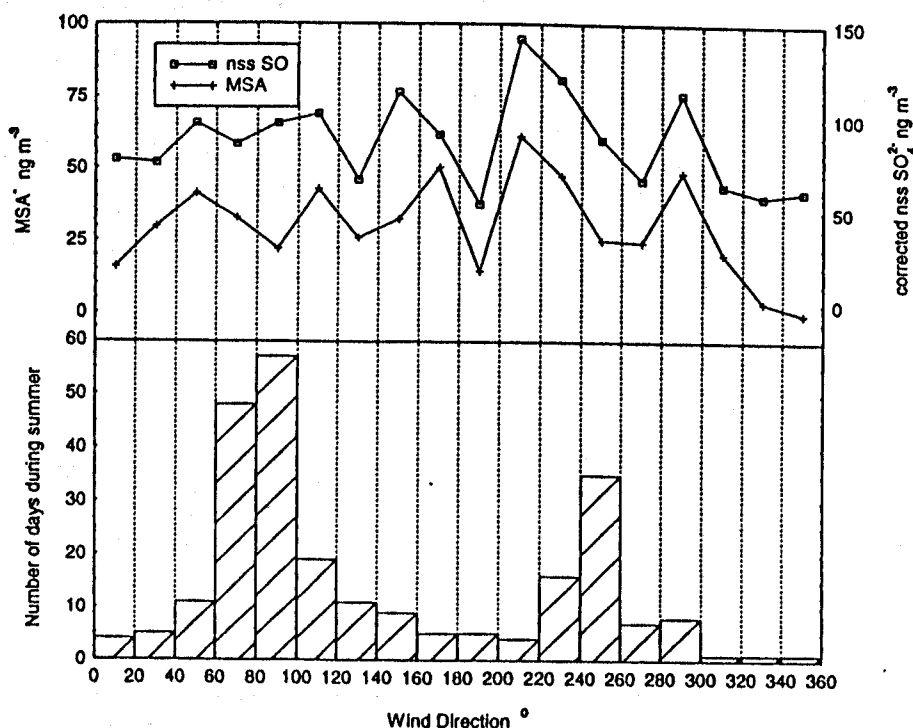


Figure 3.26a: MSA and nss sulphate [adapted from Minikin et al., submitted], concentrations in snow and ice, with distance inland from the coast.

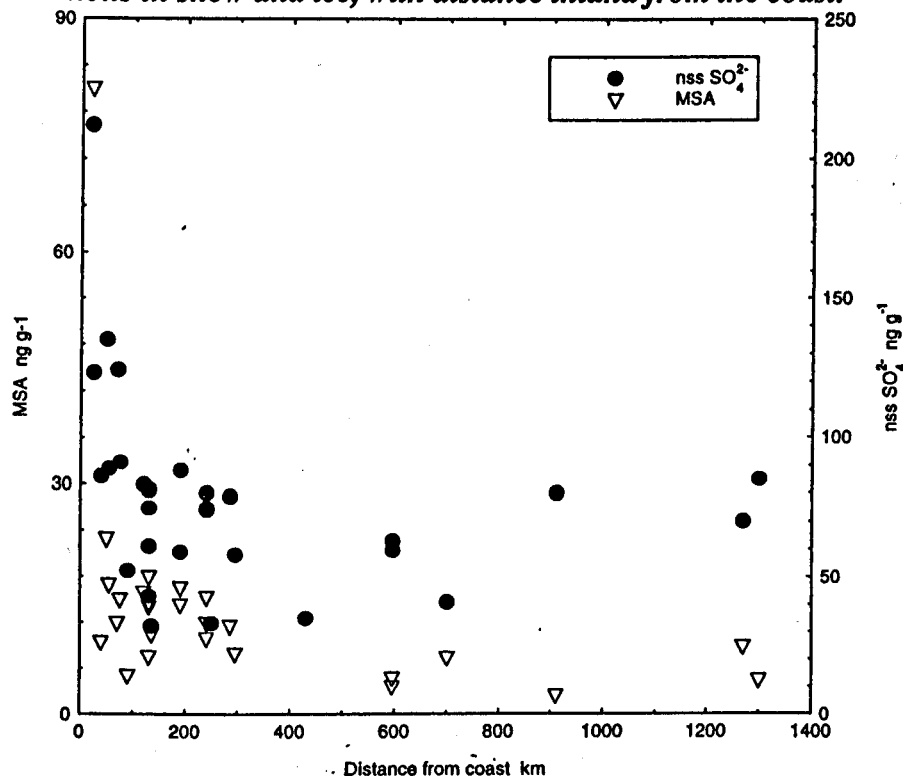


Figure 3.26b: Sea salt (chloride) concentrations [taken from Mulvaney and Wolff, 1994] in snow and ice, with distance inland from the coast.

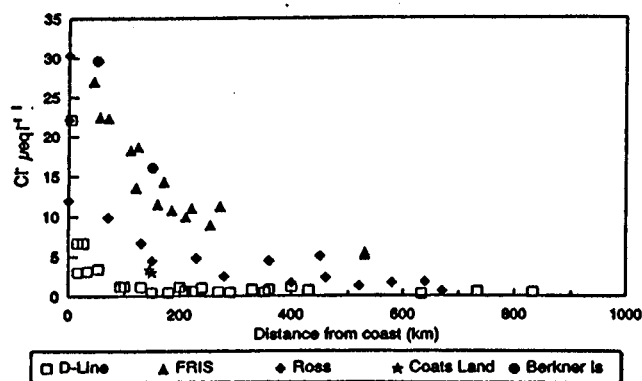


Fig. 4. The concentration of Cl^- from the French chain of D sites, the Ross Sea, the Filchner-Ronne Ice Shelf, including Berkner Island, and Coats Land plotted against distance from the coast.

Figure 3.27: Representative back trajectory classifications: continental coastal (Cc), continental interior (Ci), marine coastal (Mc) and marine open water (Mo).

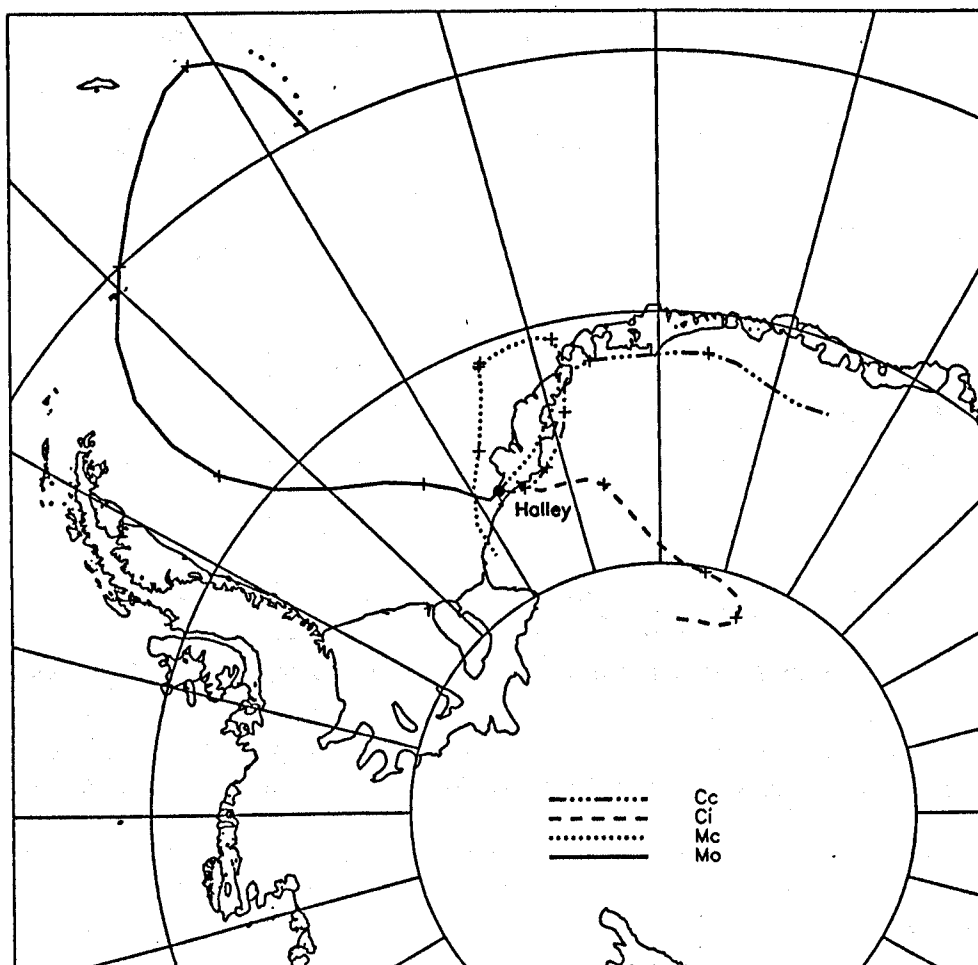


Figure 3.28: Back trajectories for the 25 February 1992, a day of high MSA concentration and the 24 February 1992, a day of low MSA concentration.

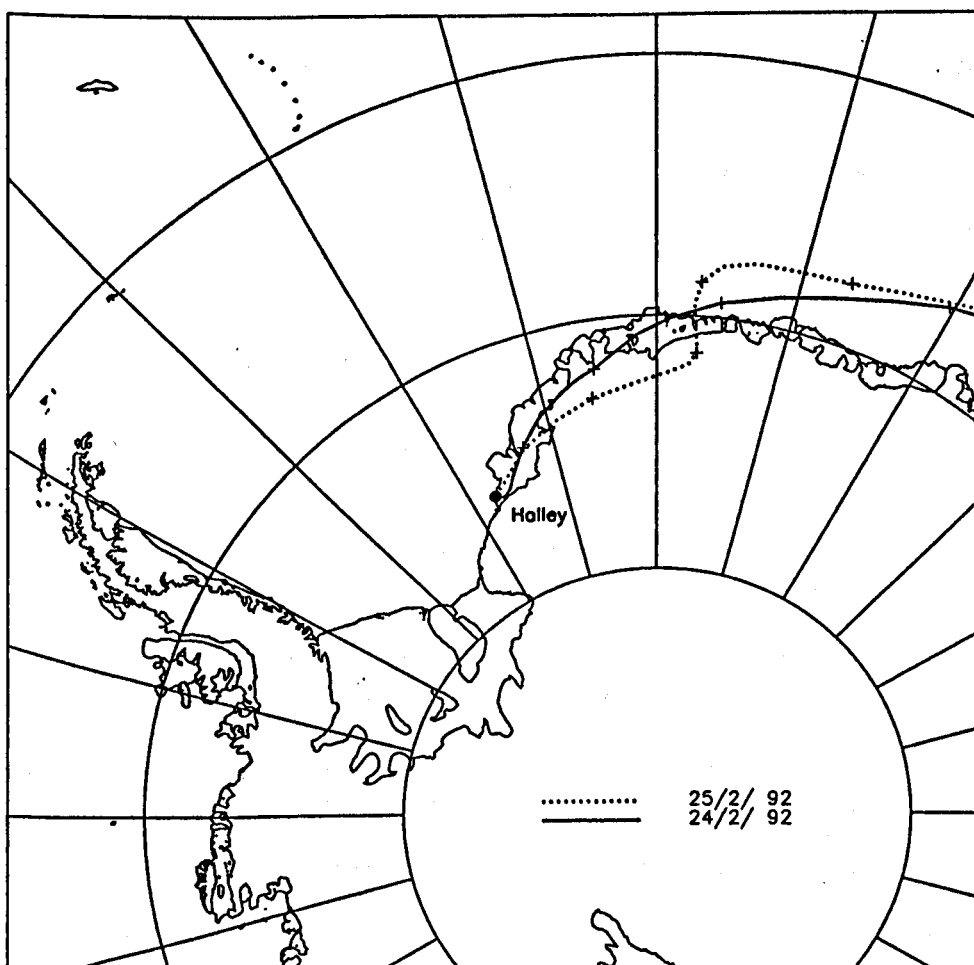
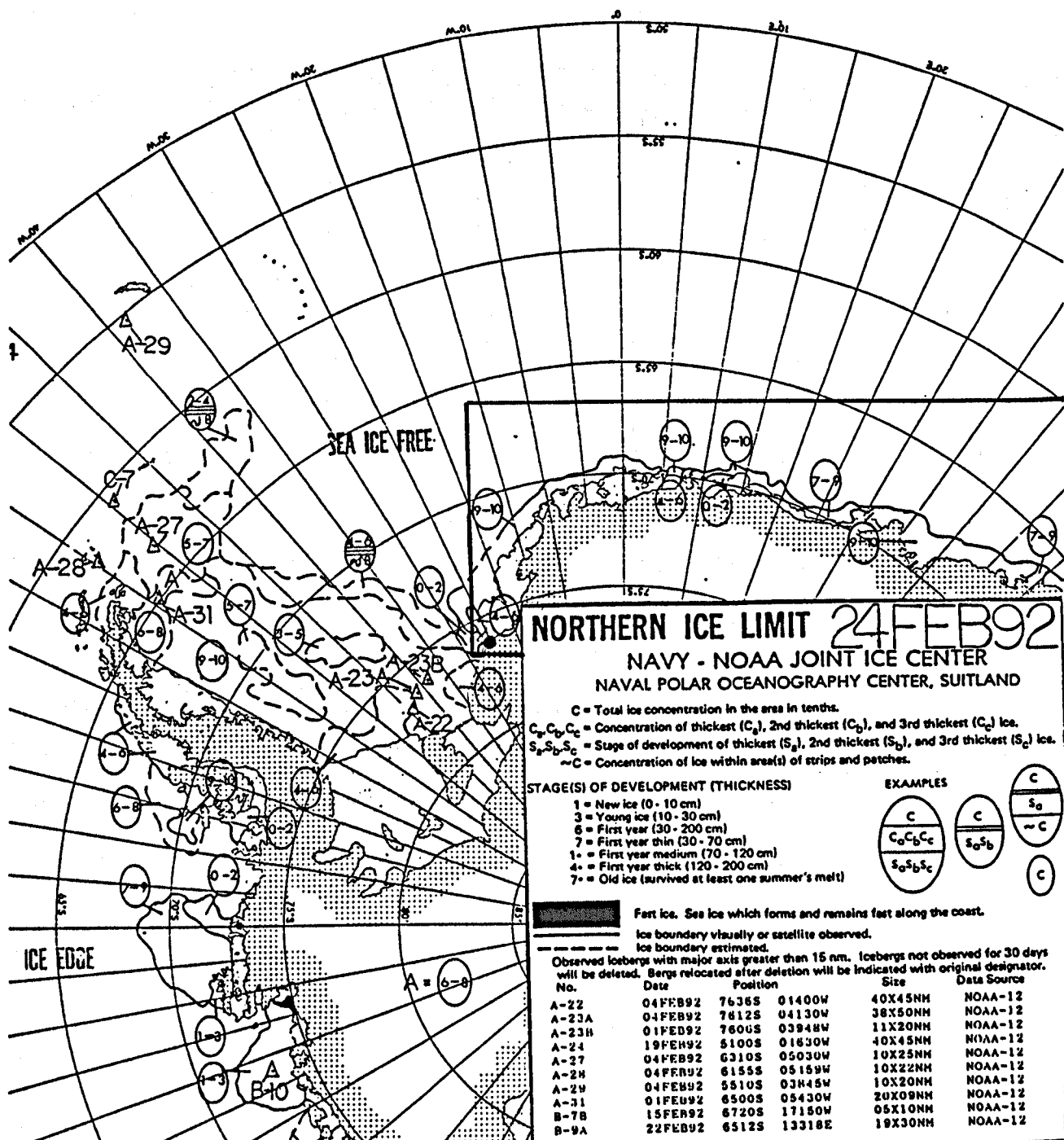


Figure 3.29: Weekly composite sea ice coverage chart for the week ending 24 February 1992



The approximate area in which the air mass travels is indicated by the box. Halley, where each trajectory is from, is marked by a solid dot, (75°35'S, 26°27'W).

Figure 3.30: Back trajectories for the 11 March 1992, a day of high MSA concentration and the 10 March 1992, a day of low MSA concentration.

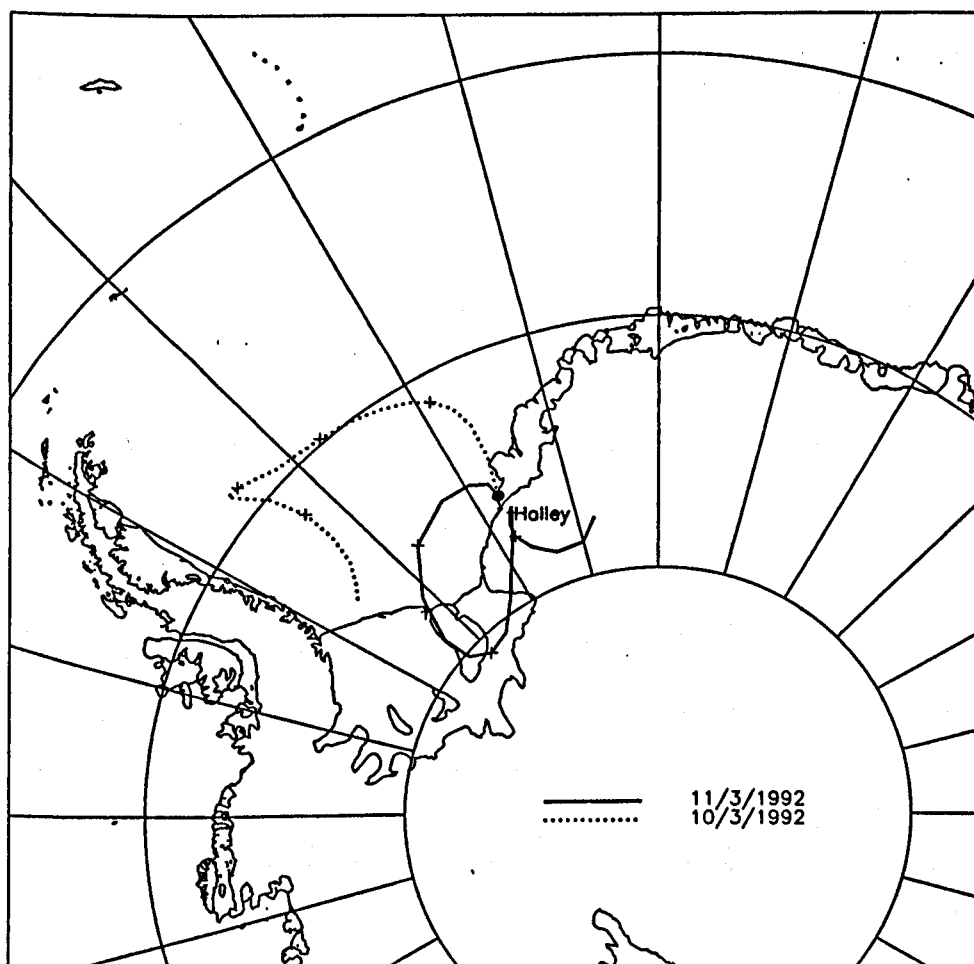
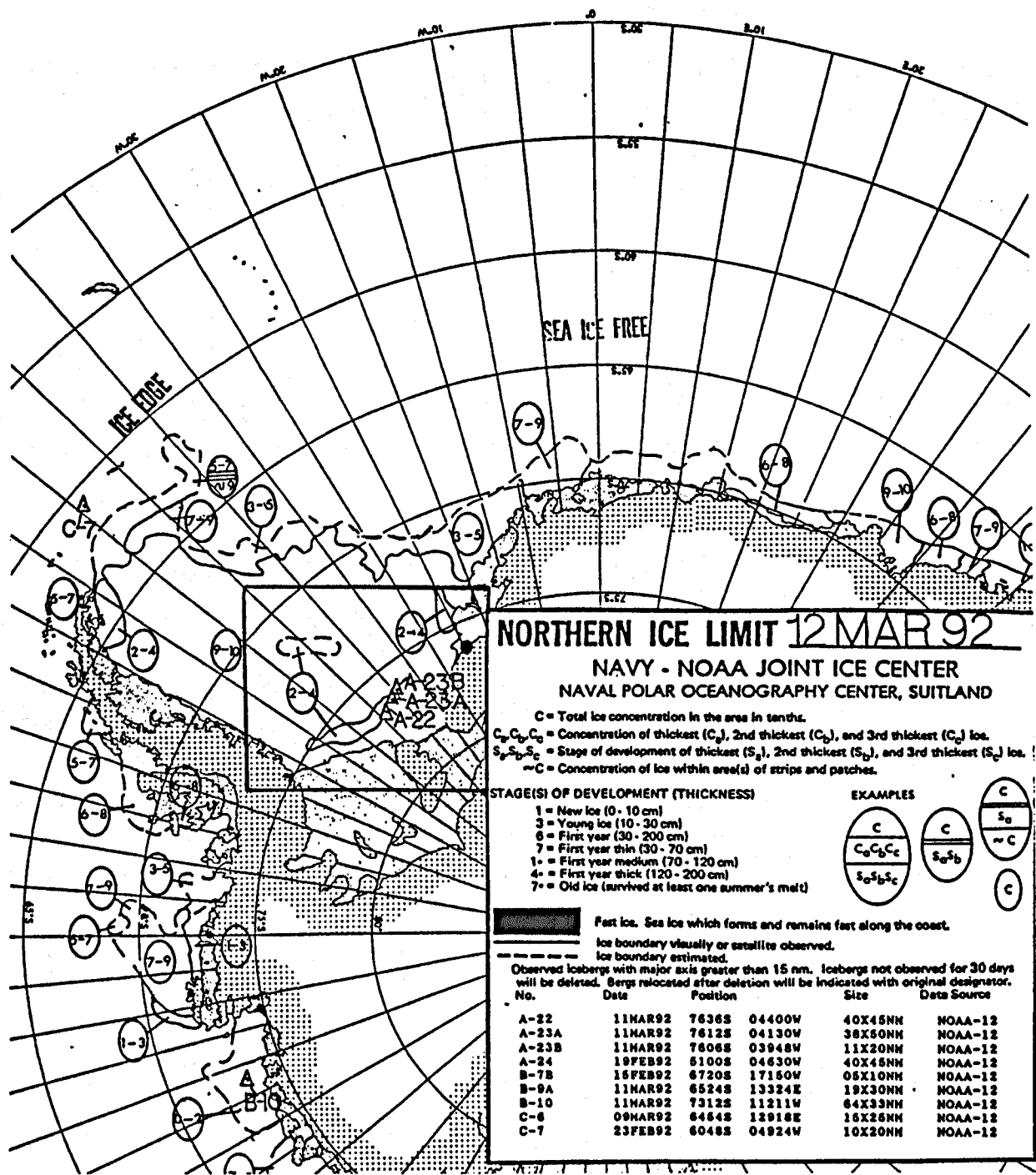


Figure 3.31: Weekly composite sea ice coverage chart for the week ending 12 March 1992.



The approximate area in which the air mass travels is indicated by the box. Halley, where each trajectory is from, is marked by a solid dot, (75°35's, 26°27'W).

Figure 3.32: Back trajectory for the 19 May 1992, a day of high sea salt concentration

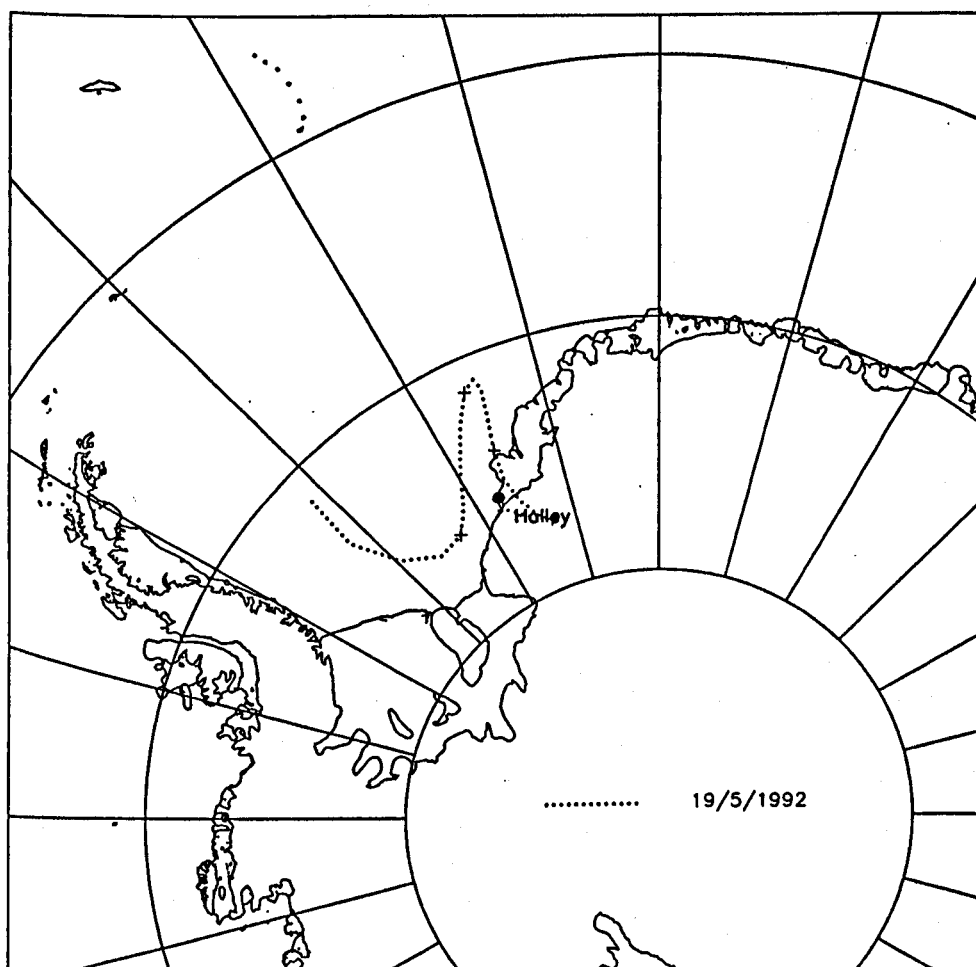
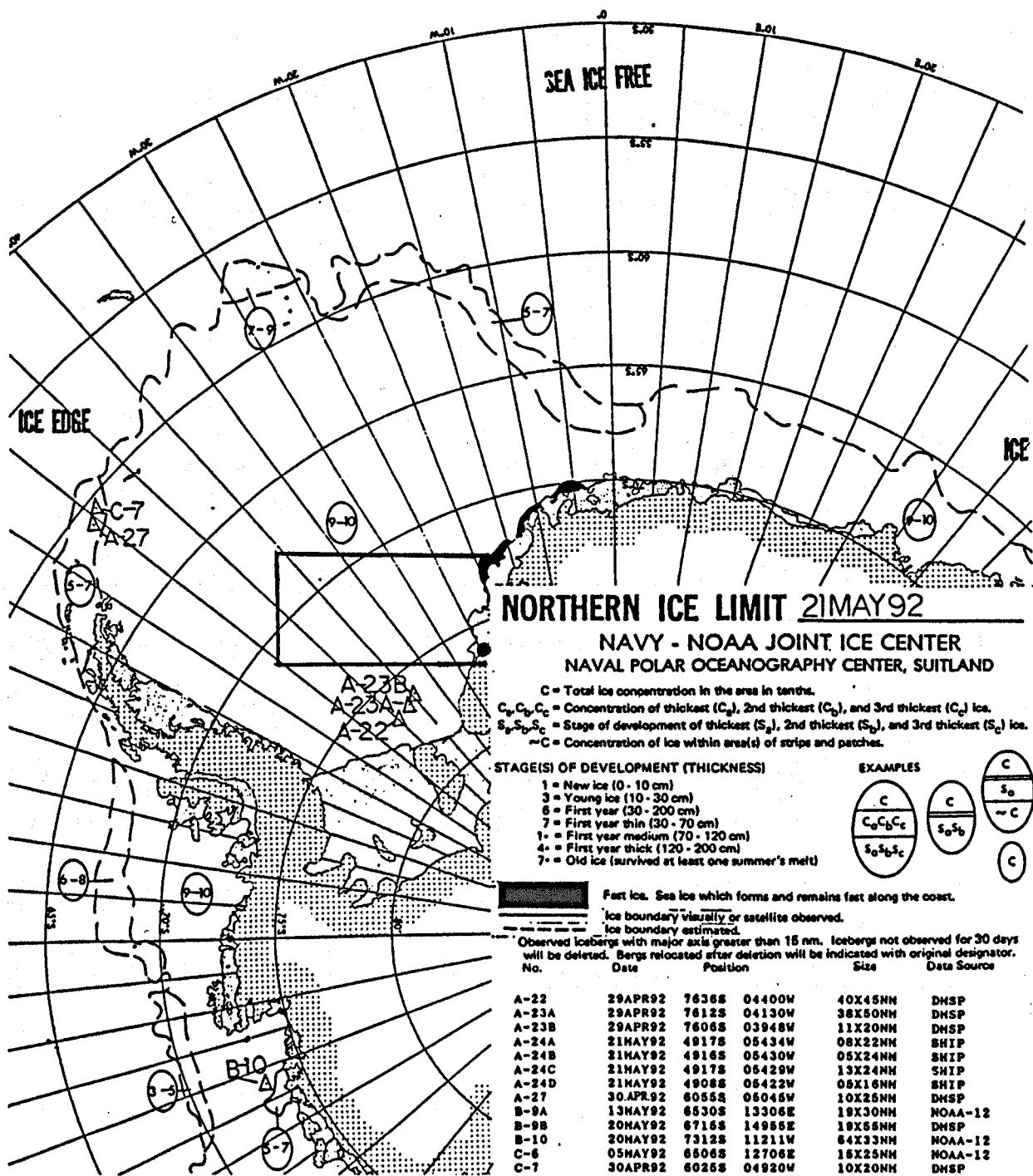


Figure 3.33: Weekly composite sea ice coverage chart for the week ending 21 May 1992



The approximate area in which the air mass travels is indicated by the box. Halley, where each trajectory is from, is marked by a solid dot, (75°35'S, 26°27'W).

Chapter 4

Snow Chemistry in Coastal Antarctica

4.1 Introduction

A knowledge of the chemistry of Antarctic snow is crucial to the interpretation of ice cores. Snow chemistry needs to be understood in terms of how concentrations of species in snow relate to concentrations in air, how these species are deposited and what happens to them after reaching the surface.

The aim of this work is to increase our understanding of Antarctic snow chemistry. In this chapter we will look at the seasonality of sea salt species, non sea salt sulphate and methanesulphonic acid in surface snow. These will be compared with aerosol concentrations also measured at Halley. Some specific events in the daily sampled, surface snow data will be discussed in detail. Spatial variability will also be discussed in this chapter.

4.2 Snow Sea Salt

Two simultaneous collections of surface snow samples were made at Halley (using a

specially prepared device). One sample was collected from the first 10 mm of snow and a second, sampled from 3-15 mm below the surface (see section 2.9 for more information on sampling procedures). However in practice, due to natural undulations in the snow surface, the same depth of snow may be sampled in both cases. For the purpose of describing seasonality in the snow record, and in general comparisons with aerosol species, the concentrations of these two snow samples have been averaged. It should be noted that the snow samples described in this chapter refer to **surface** snow collections only. Accumulated snow, which was also sampled, is discussed elsewhere in sections 5.8c and chapter 6.

4.2.a Seasonality

The annual mean for sea salt surface snow concentrations at Halley is 1358 ng g^{-1} . As daily sampled snow data such as this, are relatively sparse in Antarctica, it is difficult to compare annual mean concentrations. The majority of snow collections are made from pits [Whitlow et al., 1992; Legrand & Delmas, 1984; Delmas et al., 1982; Aristarain & Delmas, 1981], and make no attempt at sampling fresh snowfall events. Other sampling programmes have focused on how near-surface concentrations drop off with distance inland, from the coast [Dahe et al., 1992; Kamiyama et al., 1989; Legrand & Delmas, 1985]. The daily sampled, surface snow time series from Halley is therefore rather unique for Antarctica.

Looking at the time series for sea salt in snow (figure 4.1, lower plots), this clearly does not

follow a definite cycle. A strong peak is seen during winter 1991, but this signal is not repeated during winter 1992. Despite elevated concentrations during late June and early July for a few individual days, monthly averages show little difference between these winter values and summer 1992. The mean concentration for winter 1991 is 1893 ng g^{-1} . This does not compare well with the mean winter 1992 value, when concentrations averaged at 872 ng g^{-1} , a factor two lower. The absence of a winter 1992 maxima is also marked in comparison with the strong seasonal cycle seen in the aerosol record (figure 4.1, upper plots), and indicates that the relationship between Antarctic aerosol and snow chemistry is not simple.

It is possible that the missing winter 1992 peak could be attributed to large scale spatial variability in the snow record (see section 4.10). The fact that Halley base, and the snow and aerosol sampling campaigns, were relocated a further 14 km inland after the 1991 collections, may cause differences between the years. This would be particularly so if we assume that the source of winter sea salt is a very local one. A change in sampling site of 14 km could affect concentrations considerably (see section 1.5.a for details). However, as the sea salt aerosol record does not lack the winter 1992 peak, this explanation seems unlikely. Differences in the snow record between years, may simply be the result of changes in the deposition fluxes of chemical species from the air, to the snow surface, with processes that dominated in winter 1991 being different from those in 1992. Due to the episodic nature of the aerosol time series, an aerosol signal will only show up in the snow record if efficient deposition processes exist. Later in this thesis, the fluxes for the deposition of species to the surface, and the processes by which aerosols are removed from

the atmosphere, will be examined in an attempt to quantify the dominant deposition processes at work in coastal Antarctica.

A secondary, smaller maximum, is evident during summer 1992 and this may also occur in summer 1991 and 1993. Concentrations are certainly increased in December and January 1993 in both the snow and aerosol records. However, because samples are not available for the whole of these two years, this cannot be confirmed.

Figure 4.2 shows monthly snow averages for species that comprise the sea salt component, such as chloride, magnesium and potassium, which were also measured in the Halley samples. These species are seen to follow the same pattern as sea salt concentrations calculated from sodium data.

4.2.b Variability in Snow Sea Salt.

The advantage with the surface samples collected from Halley is their high resolution; the fact that they were collected on a daily basis, giving us the opportunity to look at individually high events in the data set in detail. In chapter 3 we have seen that aerosol sea salt concentrations are highly variable on a day to day basis. In comparison, the snow record seems more 'smoothed' than the aerosol seasonal cycle (figure 4.1). Marked short term variability does occur in the snow record, but the peaks are not as sharp and tend to last for several days. Elevated snow concentrations seem to be characterised by a sharp peak, but with a broader shoulder peak trailing after the sudden increase.

A smoother cycle is to be expected, as snow is continually exposed to the air and aerosol deposition, often for long periods of time. New snowfall events may persist for several days, giving a constant concentration. Drifting and blowing snow will indeed cover a surface, but re-exposure, due to scouring, or redistribution of snow elsewhere, is also common. The effect will be to make day to day comparisons between aerosol and snow concentrations difficult, but should not affect the overall seasonal trend.

4.3 High Aerosol Concentrations: are they seen in the snow record?

To see how well large inputs of aerosol sea salt are recorded in the snow data set, the ten events of particularly high aerosol concentrations, studied in section 3.4, are compared with the corresponding snow data (figure 4.3). In four events (April and June 1991, and June and July/August 1992), the high aerosol concentration leads to peaks in the snow record. However, although seen as a peak, the snow concentrations may only be increasing by a small factor (eg. April 1991 snow only increases by a factor 2) and are therefore, not necessarily recorded as significantly important snow events. Three other events (April, August and November 1992) indicate a possible delayed signal in the snow record. The remaining three high aerosol episodes give confusing signals, with April/May and May 1991 actually indicating that the snow record leads the aerosol signal. However, due to missing snow samples for April/May 1991 this may be misleading.

To investigate the broader relationship between aerosol and snow, six specific months of snow data were examined, and compared with the daily aerosol concentrations (figure 4.4).

For these months, the two data sets do appear to follow a similar pattern. The major peaks in the aerosol record are either followed by, or coincide with, peaks in the snow record.

It seems that individual inputs of elevated aerosol sea salt are not necessarily incorporated into the snow record. Over a longer scale, of a month or year, the main features of the aerosol record are generally found in the snow time series. However, with this in mind it seems surprising that the winter 1992 maximum is not strongly evident in the snow data.

4.4 High Snow Concentrations: are they seen in the aerosol record?

Six events of the highest snow concentrations were compared with the corresponding aerosol record, to see whether these episodes could be identified in the aerosol time series (figure 4.5). Of the six events, all but one high snow episode (August 1991) could be linked to a peak in aerosol concentration. Except for this one event, snow peaks either coincided with elevated aerosol values, or lag slightly behind.

It can be concluded that high snow concentrations can generally be found in the aerosol record. However, the highest aerosol peaks are not necessarily recorded in the snow. Over a longer time scale, the two records are found to compare favourably, but on an individual event basis, comparisons are harder to draw.

4.5 Fractionation of Snow Sea Salt

As already detailed in sections 3.5 and 3.8.d, evidence is mounting for the occurrence of sea salt fractionation in coastal Antarctic aerosol, snow and firn cores, particularly during the winter months. It has been suggested that this fractionation occurs before sea salt particles are incorporated into the air. Top surfaces of newly formed sea ice, containing puddles of concentrated brine in the form of slush, liquid and frost flowers, are thought to be the source of fractionated sea salt. This fractionation, which is most apparent in winter aerosol samples, is also evident in the Halley surface snow record. Figure 4.6 shows winter and summer non sea salt sulphate concentrations plotted against sodium data. Non sea salt sulphate is calculated after subtracting a sea salt component, whose concentration is determined using the traditional bulk sea water ratio of 0.252 (see sections 3.5 and 3.8.d). In figure 4.6, fractionated samples will be denoted by a deviation from the bulk sea water ratio of 0.252, shown by the horizontal dashed line. The winter values are clearly fractionated, with a negative gradient of $-0.179 (\pm 0.006)$.

Snow concentrations during summer should not show any signs of fractionation, when plotted in this way (figure 4.6), and should lie on the bulk sea water ratio line. However, it is apparent that these summer points actually tend to lie above the BSW line. This is likely to be because the summer data exhibits a large amount of scatter. Simple linear regression analysis gives a gradient of 0.228 for the summer samples, with an uncertainty value in the gradient of ± 0.02 .

In order to take into account this fractionation process, a corrected bulk sea water ratio (k^*) is needed when calculating sea salt sulphate concentrations, particularly during the winter (see sections 3.5 and 3.8.a). For Halley aerosol this was found to be 0.107 ± 0.01 (1σ) and is determined by adding the gradient of the best fit line for winter samples (when uncorrected nss sulphate is plotted against sodium, figure 4.6) to the traditionally used bulk sea water ratio. For the snow samples, k^* becomes 0.073 ± 0.006 , $(-0.179+0.252)$. Therefore, the snow value is significantly lower than the aerosol value, even at the 2σ level. The different k^* value for snow may indeed be more appropriate to use for these samples than that determined from aerosol data. This value corresponds almost exactly with the chosen aerosol k^* used at Neumayer and Dumont D'Urville of 0.075 [Minikin et al., submitted]. The fact that k^* values differ between aerosol and snow, and that snow samples seem to be more fractionated, indicates that additional fractionation may occur once aerosols are deposited on the snow surface.

4.6 Snow Sulphur Species

Earlier in this chapter and in sections 3.5 and 3.8.d, the method for determining nss sulphate has been discussed. The traditionally used bulk sea water value of 0.252 is no longer thought to be applicable, particularly in coastal Antarctica. For the purpose of this study and when referring to Halley snow samples, corrected nss sulphate values will be used throughout the year, using 0.073 as the bulk sea water ratio. The effect of using this corrected BSW ratio during summer, when fractionation is not likely to occur, is minimal (see section 3.8.d for more detail). This is because the sea salt signal at Halley is weak

during the summer and therefore the presence or absence of fractionation only slightly influences the calculated non sea salt sulphate concentrations. Also, temperatures at Halley during the summer can still fall below -8.2°C , the temperature below which fractionation is expected to occur [Wagenbach et al., in press].

4.6.a Seasonality

Figure 4.7 shows the daily raw concentrations and monthly means for corrected snow non sea salt sulphate (lower plots) in surface snow at Halley. (Also shown are the corresponding aerosol time series (upper plots) for comparison). The annual mean for corrected non sea salt sulphate is 239 ng g^{-1} . This compares with 164 ng g^{-1} for non-corrected nss sulphate, calculated using a BSW ratio of 0.252. The two nss sulphate plots are shown together in figure 4.8. As in the aerosol record, using a lower bulk sea water ratio eliminates some of the adversely negative winter nss sulphate values, but does not significantly alter the seasonal cycle.

The annual mean for methanesulphonic acid in surface snow is 56 ng g^{-1} . Figure 4.9 shows the daily raw concentrations and monthly means (lower plots), with corresponding aerosol time series (upper plots) shown for comparison.

As in the case of snow sea salt, there are relatively few nss sulphate and MSA surface snow records. De Mora et al, [1997] collected surface snow and pit samples from the East Antarctic plateau over a period of two months during summer, and found concentrations

for nss sulphate ranged from 72-89 ng g⁻¹. For MSA, concentrations ranged between 7-9 ng g⁻¹. These concentrations are considerably lower than those for Halley, where mean summer nss sulphate values are 428 ng g⁻¹ and 119 ng g⁻¹ for MSA. This considerable difference reflects the short time period in the De Mora study.

The strong seasonal cycle seen in the aerosol records for nss sulphate and MSA is repeated in the surface snow records. Both species strongly peak during summer. However, they appear to have their maximum concentrations a month earlier in the snow record, than in the aerosol. This seems unlikely and is probably due to the missing aerosol data points at the end of January 1992. Much higher concentrations are evident in the aerosol record for January 1991 and 1993, than 1992.

4.6.b Variability in Sulphur Species

Daily variability in snow nss sulphate and MSA is highly comparable to that seen in the aerosol record. Variability is less marked than sea salt, and high concentrations tend to last for several days, rather than sporadic, sudden increases. A less spiky time series is to be expected for nss sulphate and MSA, as their longer range source (see sections 3.9.a and 3.11) gives the species time to homogenise before deposition to the snow surface.

4.7 High Aerosol Concentrations: are they seen in the snow record?

In order to investigate how well sulphur species are recorded in the snow record, from the air, the eight cases of particularly high aerosol MSA which were studied in section 3.10, are now examined here. As the majority of sulphur in coastal Antarctica is biogenic in origin and MSA only has a biogenic source, MSA is chosen to be representative of the sulphur species in this area. Figure 4.10 shows high MSA aerosol concentrations and corresponding snow values. As for sea salt, a visual inspection of the individual episodes of high MSA appears to offer a weak relationship between the aerosol and snow records. Two events (March and 9-14 December 1992) do have corresponding aerosol and snow peaks. The snow record for February, 21-26 December 1992 and 3-10 January 1993 appears to peak just after the high aerosol episode. For the remaining three events it is not obvious whether the aerosol peak is also seen in the snow. Monthly comparisons are more convincing (figure 4.11) and indicate that variability is not always mirrored in the snow record and longer time scale comparisons are essential.

4.8 High Snow Concentrations: are they seen in the aerosol record?

Six events of the highest snow concentration were then compared with corresponding aerosol record, to see whether these episodes could be identified in the air time series. All the high snow events examined could indeed be identified in the aerosol record. Snow peaks either corresponded to an increase in aerosol concentration, or the signal was slightly delayed (figure 4.12).

It can be concluded that high snow concentrations for both sea salt and MSA (biogenic

sulphur species) can be traced back to the aerosol record. However, the highest aerosol inputs are not necessarily seen in the snow record. Over a long time scale, of the order a month or a year, the two records (snow and aerosol) compare well. This is particularly so for MSA and non sea salt sulphate which are driven by a very strong seasonal cycle.

4.9 General Relationship Between Aerosol and Snow Chemistry

This chapter has established that high aerosol loadings are not always recorded in the surface snow. There must be special conditions that enable aerosol deposition to occur and these processes are discussed, and quantified in chapter 5. In chapter 5, wet deposition is found to be the most dominant process for coastal Antarctica. To verify this statement, the significant weather record for Halley, was compared with the events of particularly high snow concentrations (Figure 4.3 & 4.10). As expected, in most cases, high salt and nss sulphate snow concentrations are also associated with snowfall events. However, there are many occasions throughout the year when high aerosol loadings and snowfalls occur, but without leading to an increased snow concentration. This is because other processes, such as snow redistribution due to blowing and drifting snow, can remove a snowfall once deposited.

4.10 Spatial Variability

As two, daily surface samples were taken within a few centimetres of one another (see section 2.9.b(i)), it is possible to assess their reliability and representability. Any small

scale variability will also be seen in the comparison of these samples.

Figure 4.13 shows the two Halley snow samples plotted against one another. It was intended that sample s1 was collected from the upper 10 mm of snow and s2 slightly below this, from between 3-15 mm. However, in reality due to the natural undulations of the Antarctic snow surface, it is likely that both samples were taken from the same depth. Figure 4.13 shows that for all species of interest to this project (sea salt, MSA and nss sulphate), both s1 and s2 samples are well correlated. MSA has an almost 1:1 ratio between the two samples, with a gradient of $0.9 (\pm 0.01)$. The sea salt plot has a gradient of $0.8 (\pm 0.02)$ as does corrected nss sulphate, implying that for these species, s1 samples have a slightly higher concentration than s2. For all ions, the average difference between the two samples is found to be approximately between 10-20%.

Although spatial variability between samples s1 and s2 is small, comparative samples collected at distances over a few cm's, can have significant variability, with as much as 60% in some cases at Halley [Pasteur, 1996]. This value also corresponds to work in Greenland, where spatial variability was found to be on a similar level [Dibb, 1996; Steffensen, 1996]. In all cases, the variability could be due to drifting, or blowing snow only covering some parts of an area. The covering of drifted snow, will be both newer, softer and easier to sample, whilst other parts of the same area are left with an older, and harder snow covering. At Halley, each new, daily surface snow collection was made a few centimetres upwind of the last, to prevent contamination. It is conceivable that different ages of snow were sampled between days. This theory is reinforced as both s1 and s2

samples are found to give very similar values and yet between consecutive days, when no accumulation occurred, concentrations vary considerably (Table 4.1).

Table 4.1: Sea salt concentration (ng g^{-1}) in samples s1 and s2.

Date	s1	s2	Date	s1	s2	Date	s1	s2
10 Dec 91	794	799	14 Jun 91	713	536	26 Feb 92	280	232
11 Dec 91	1109	1267	16 Jun 91	9303	9557	27 Feb 92	1315	603
12 Dec 91	1447	2853	17 Jun 91	9050	8846	28 Feb 92	3299	3469

Larger scale variability, of several kilometres, may also effect the Halley samples. The base and sampling schemes were relocated a further 14 km inland, in early 1992 (see section 1.5.a). It could be argued that this may account for the differences in the snow record between 1991 and 1992. For the case of sea salt, the absence of a winter maximum during 1992 could be attributed to a change of site. However, as no appreciable differences were found in the aerosol record this seems unlikely.

It can be concluded that only small scale spatial variability is likely to effect the Halley snow samples. This will be in the order of between 10-20% difference between samples.

4.10.a Drifting Snow Experiment

The amount of spatial variability can be further assessed by studying the chemistry of drifting snow samples, collected from Halley during 1993. This experiment is described in detail in section 2.11.a, but briefly, nine surface snow samples were collected from a series of stakes, spaced at increasing distances apart. The distances between each stake

were, 0 cm, 5 cm, 5 cm, 20cm, 20 cm, 2 m, 2 m, 20 m and 20 m. Sample collection occurred after an event of drifting snow was recorded at Halley. Three sampling campaigns were undertaken throughout the year, with approximately 8 days worth of samples collected from each event.

Figure 4.14 shows sea salt concentration in surface snow at each of the nine stakes, after three events of drifting snow were reported. The lower figure shows that for all three events, snow at stakes 8 and 9 is very different, with concentrations differing by approximately 65%. The average percentage difference from stake to stake, for all the samples collected, is 43%. Despite this, at both of these stakes individually, the snow concentration is almost identical for each of the three events. This implies that the same snow surface was sampled on all three days and reinforces the theory that drifting snow can introduce areas of new, softer snow and yet still leave patches of older, hard snow. It seems that stakes 8 and 9 (and also possible stake 5) represent the older snow surface in these examples. In contrast, stakes 1-4 vary in concentration with space, and are likely to be new inputs of drifted snow. In the upper plot of figure 4.14, for each of the three events, stakes 5 and 9 appear to be sampling the same surface, indicating that at these locations there may be a hard, icy surface that has persisted for nearly 3 months. The drift event on 14 July is interesting as it does not appear to suffer from spatial variability. In this case a uniform deposition of new snow, with a uniform concentration has occurred.

In conclusion, the results from the drifting snow study shows two things. Firstly, spatial variability at the site does exist for distances over a few centimetres. This corresponds with

findings in the previous section. Secondly, drifting snow can dramatically add to this spatial variability, by introducing different vintages of snow.

Figure 4.1: Lower plots show daily, raw sea salt concentrations in surface snow (solid line) and monthly averages (bar graph). Upper plots show the aerosol records for comparison.

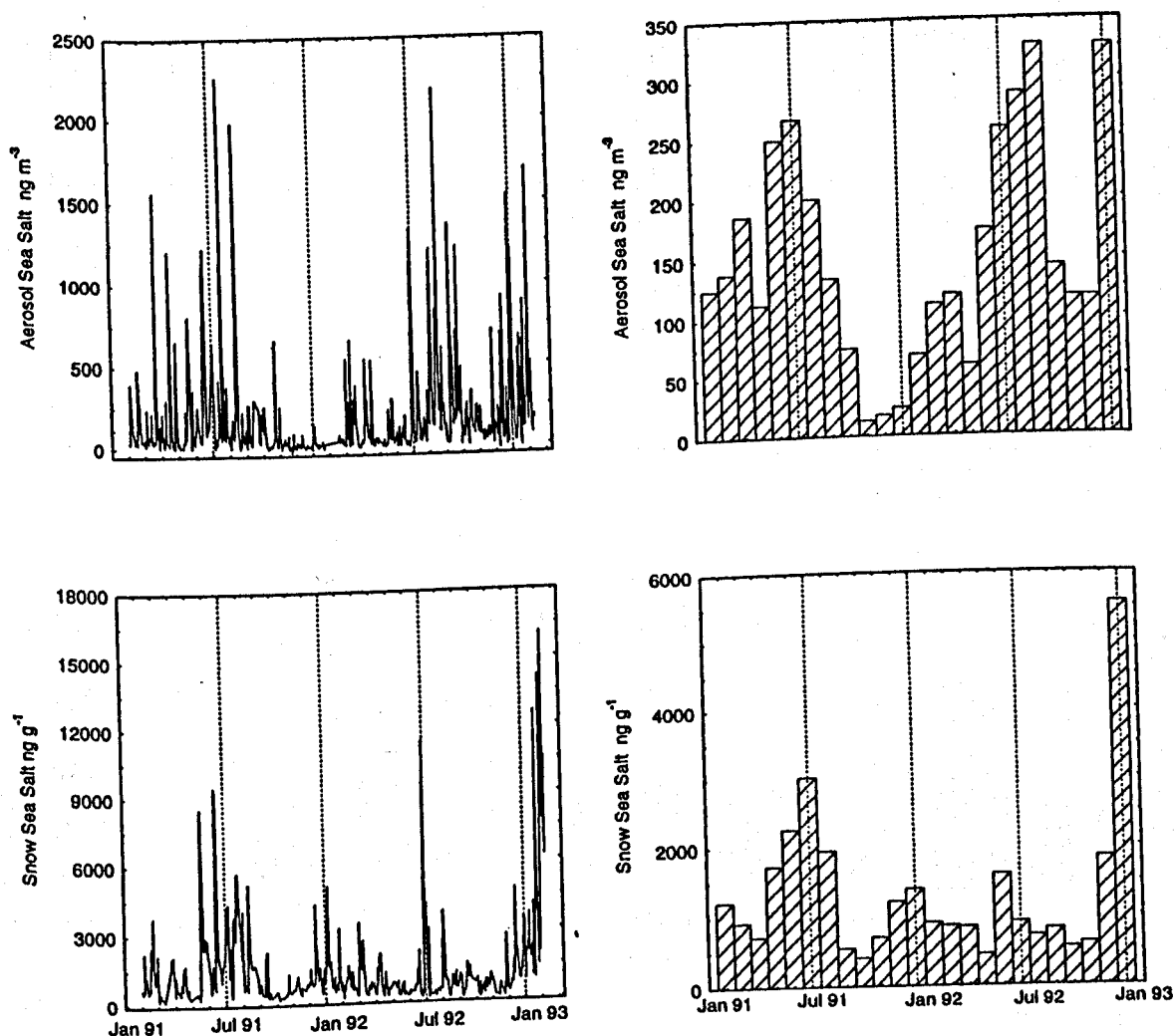


Figure 4.2: Monthly averages for snow sea salt components measured at Halley.

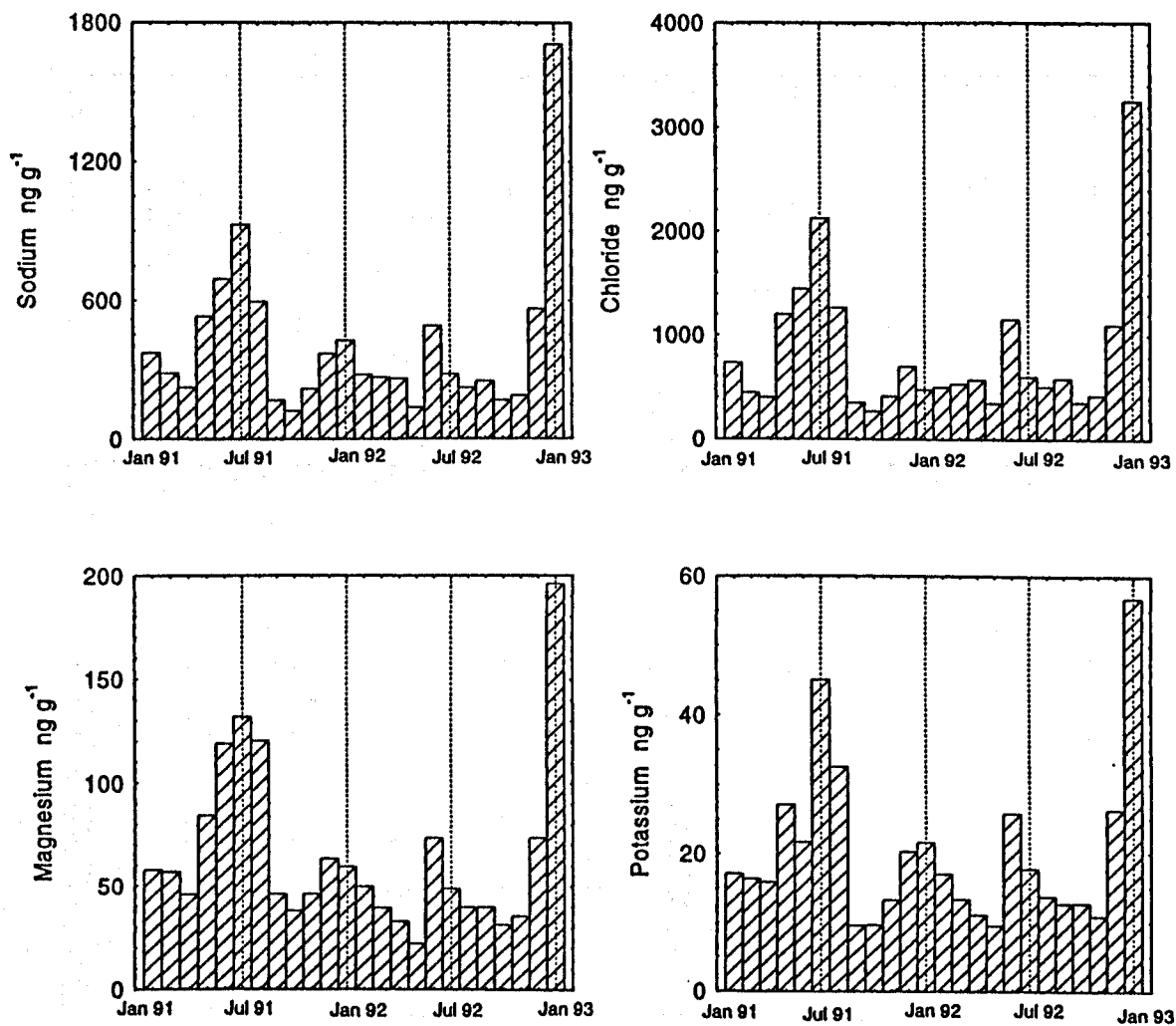


Figure 4.3a: Individual events of the highest aerosol (dashed line and squares) sea salt variability and the corresponding snow (solid line and triangles) concentrations for those days in 1991.

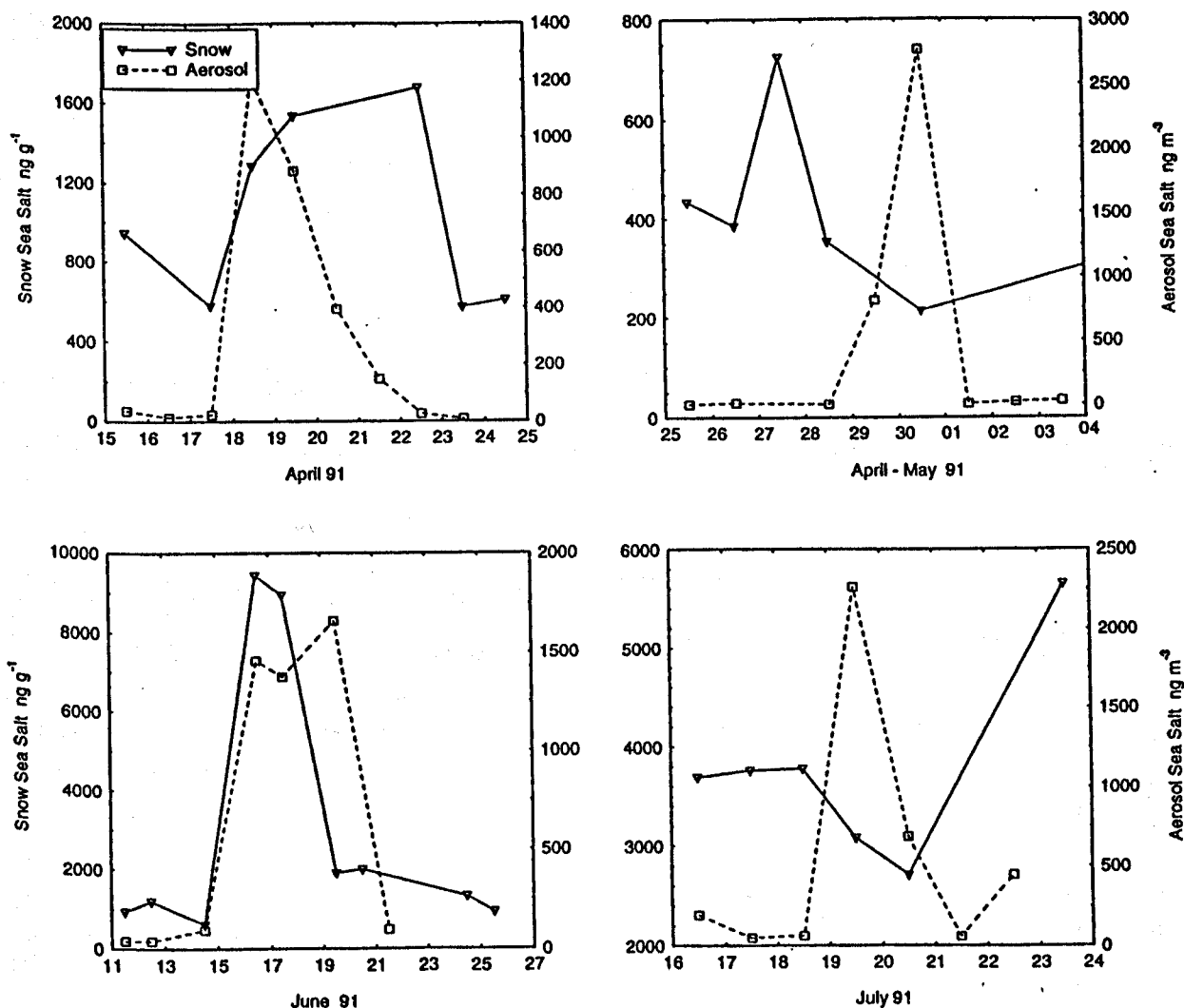


Figure 4.3b: Individual events of the highest aerosol (dashed line and squares) sea salt variability and the corresponding snow (solid line and triangles) concentrations for those days in 1992.

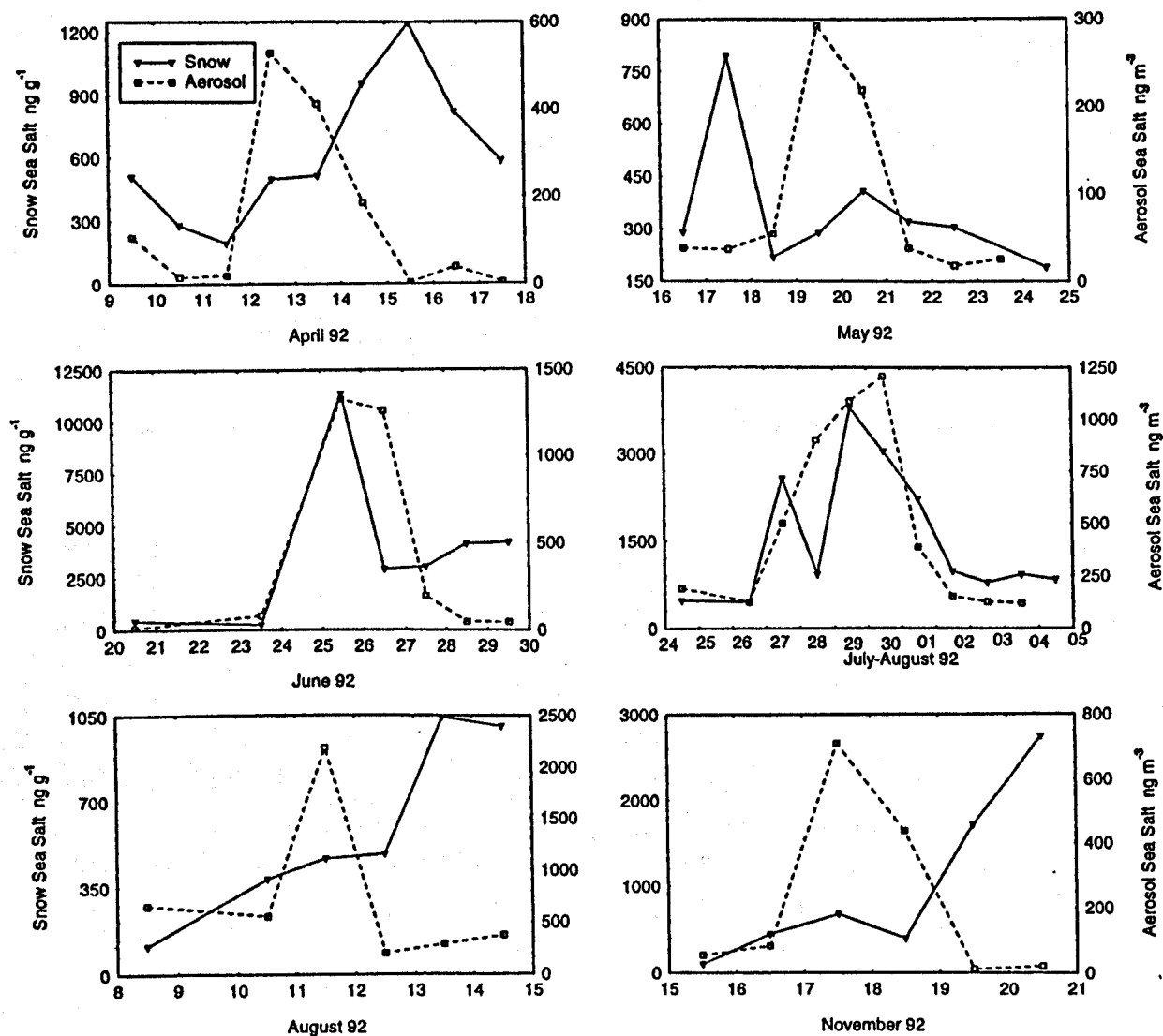


Figure 4.4: Closer examination of daily aerosol (dashed line and squares) and snow (solid line and triangles) sea salt concentrations at Halley, looking at specific months in the time series.

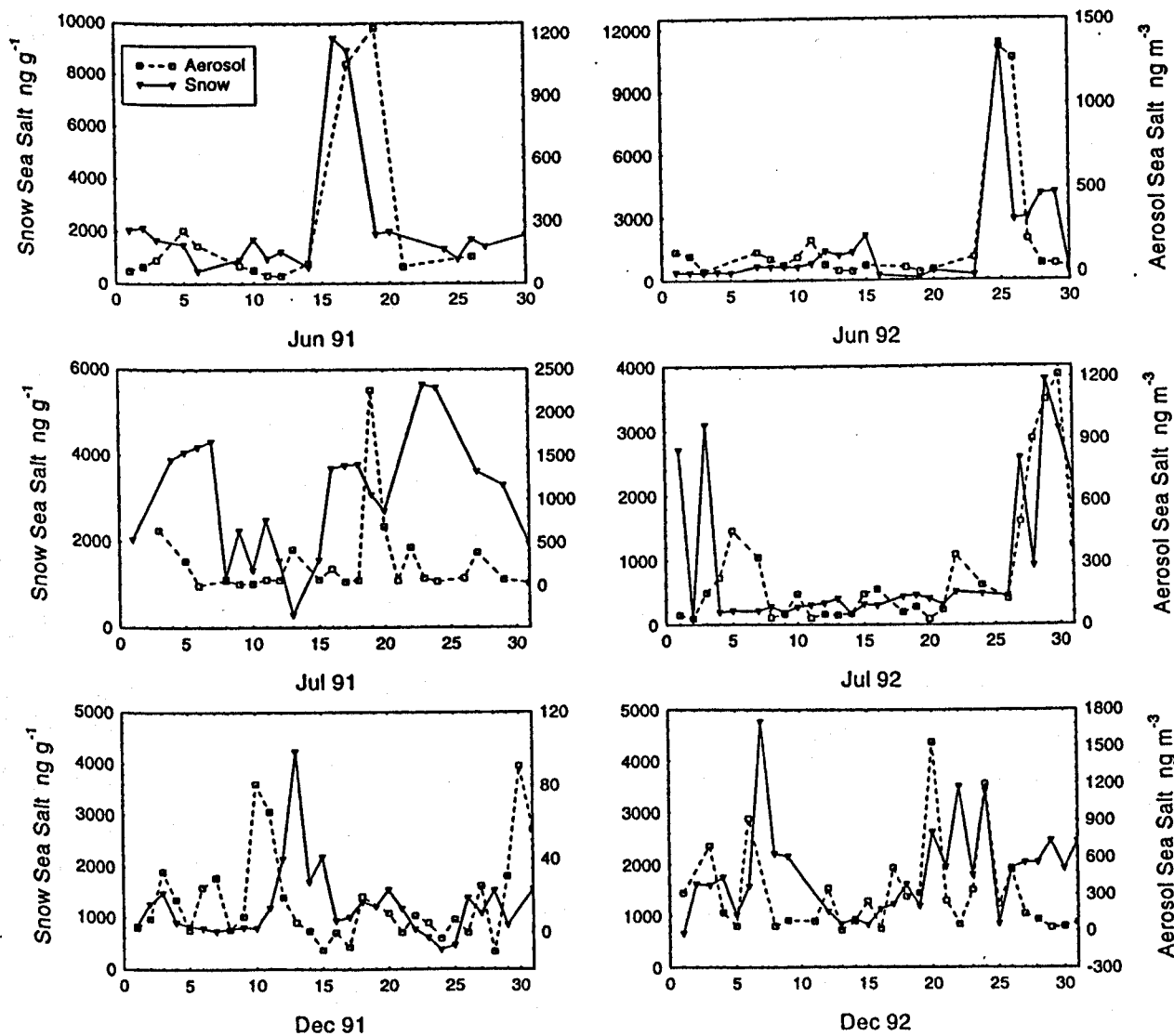


Figure 4.5: Individual events of the highest snow (solid line and triangles) sea salt variability and the corresponding aerosol (dashed line and squares) concentrations for those days.

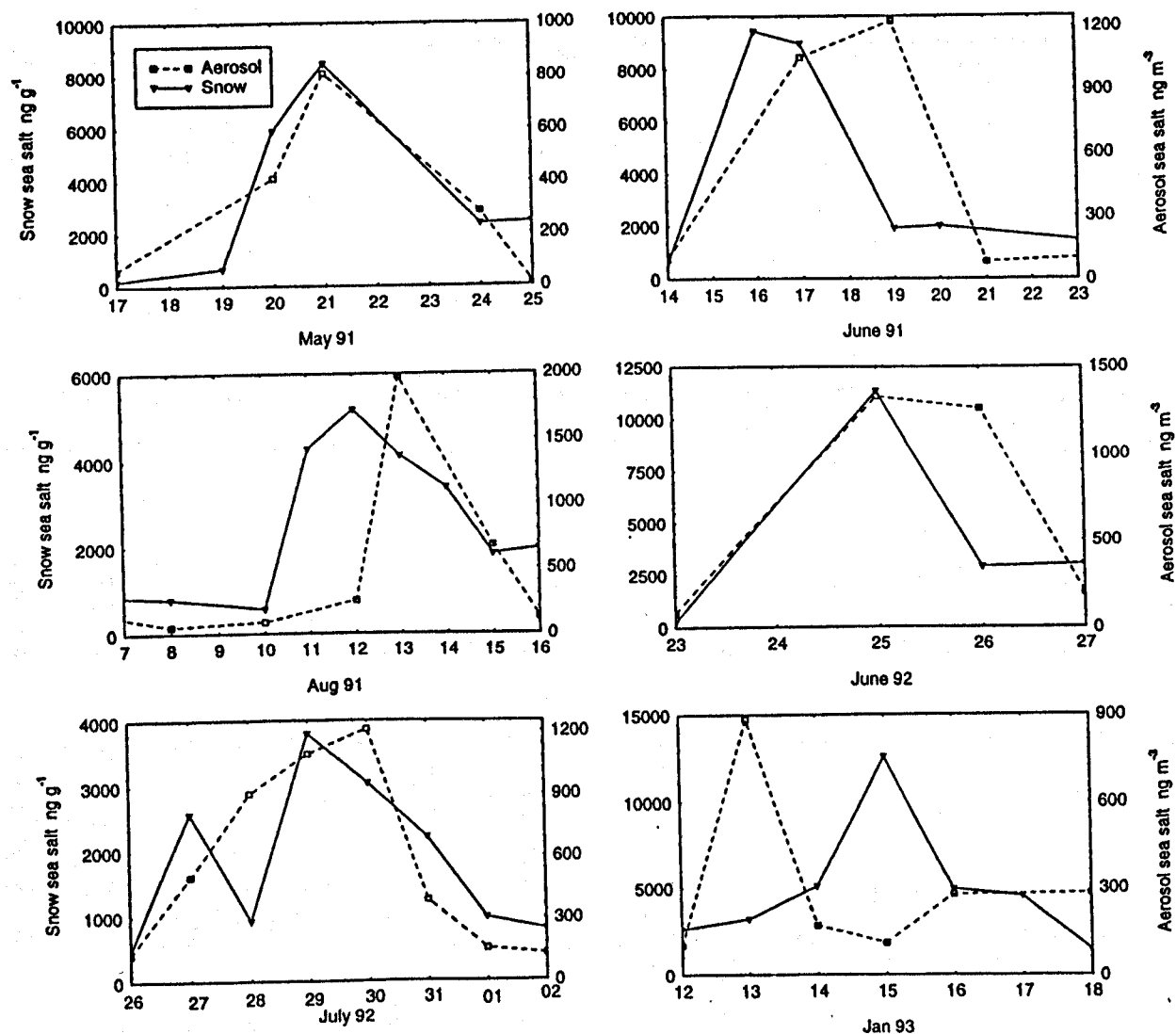


Figure 4.6: Scatter plot for non sea salt sulphate (calculate using sodium data and assuming $[SO_4^{2-}]/[Na^+]$ to be in bulk sea water ratio) versus sodium for the complete Halley aerosol record. Winter values shown as filled triangles and summer points as crosses. The bulk sea water ratio of 0.252 is shown as a horizontal dashed line, through zero.

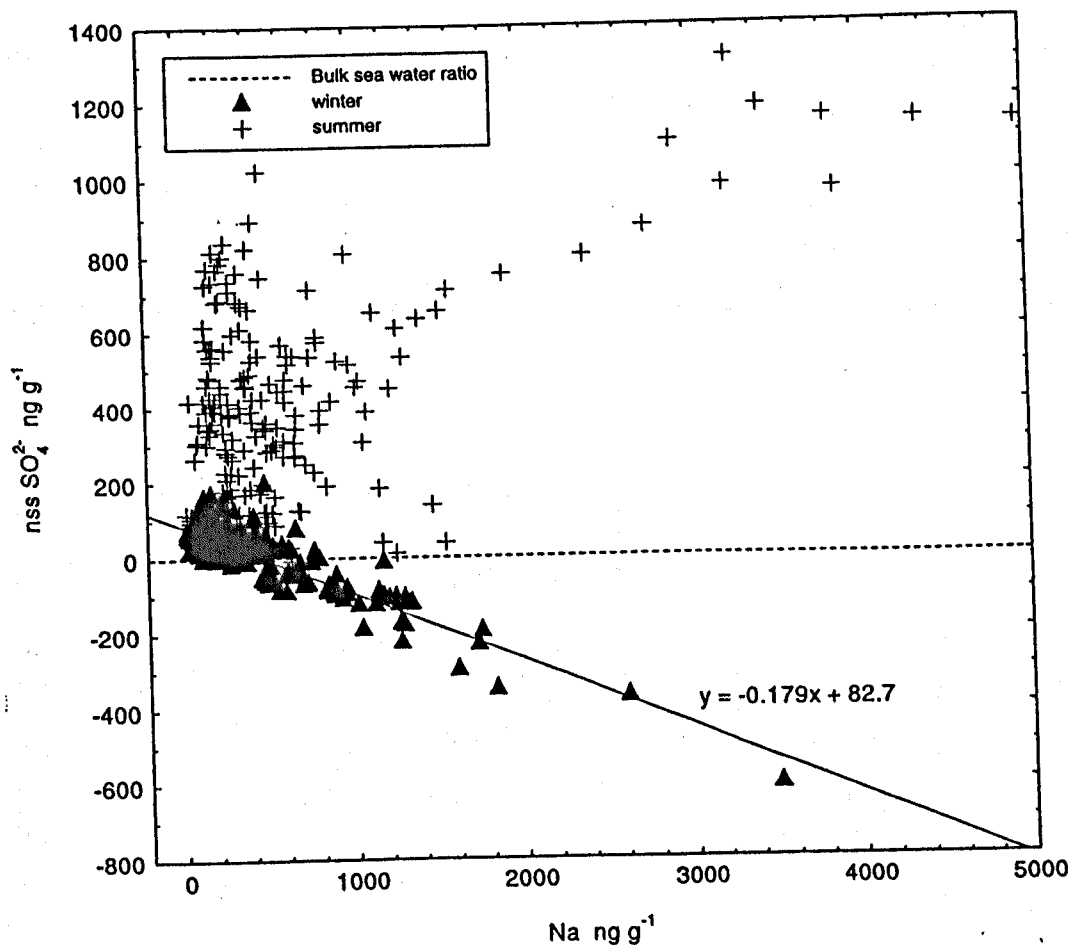


Figure 4.7: Daily raw non sea salt sulphate concentrations in surface snow at Halley (solid line) and monthly averages (bar graph), both shown in the bottom plots. Upper plots show the aerosol records for comparison.

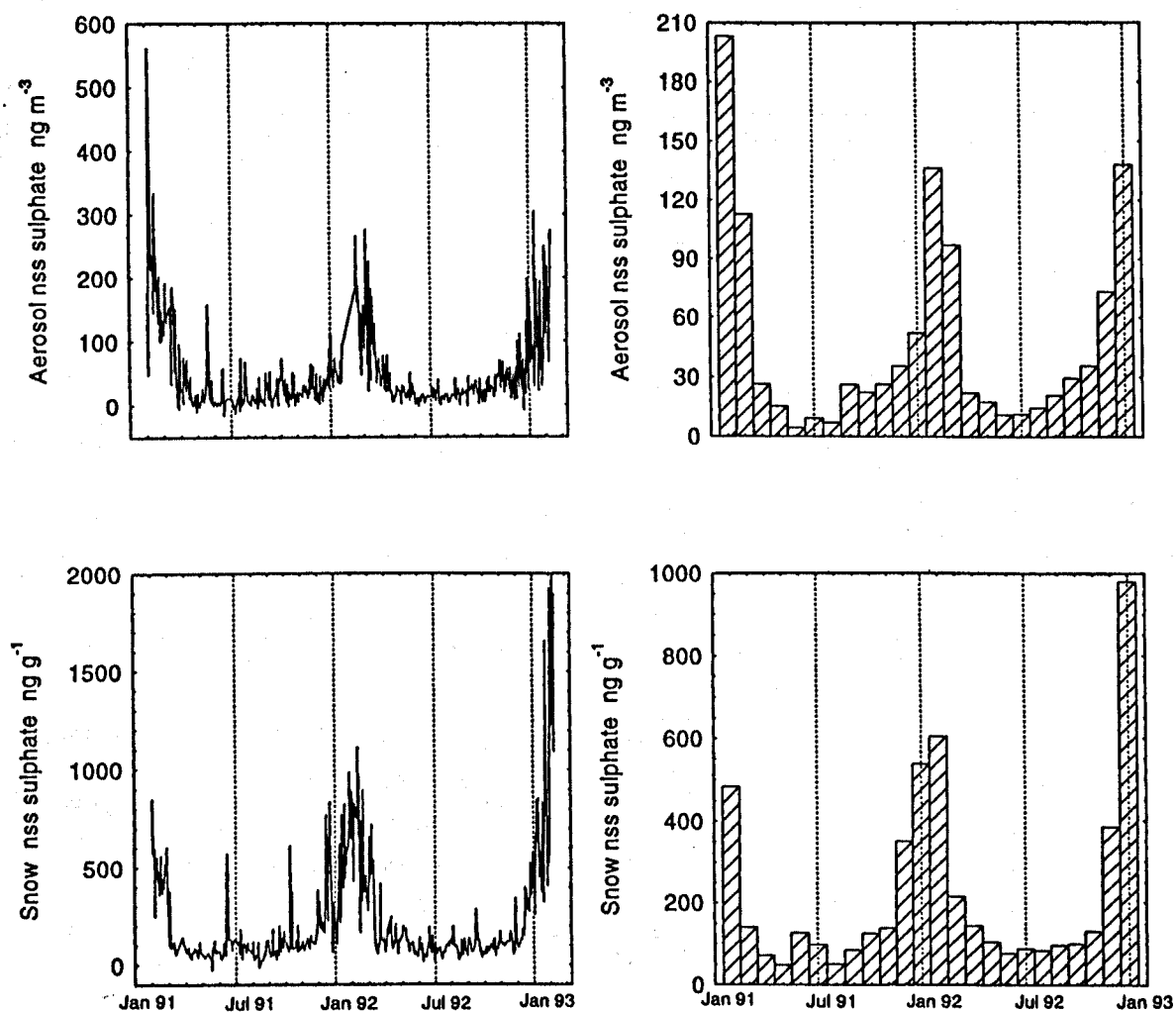


Figure 4.8: *Corrected daily nss sulphate (upper plot) and traditionally calculated nss sulphate (lower plot).*

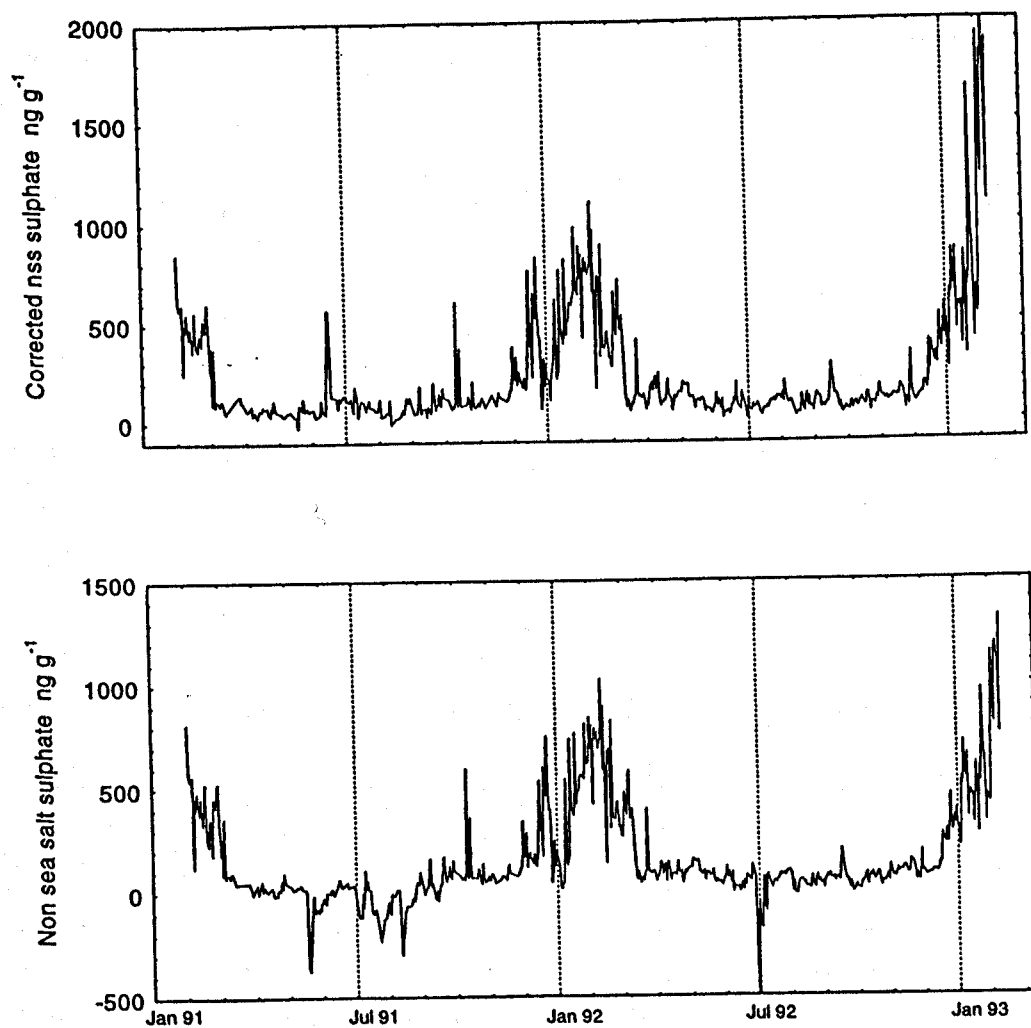


Figure 4.9: Daily raw MSA concentrations in surface snow at Halley (solid line) and monthly averages (bar graph), both shown in the bottom plots. Upper plots show the aerosol records for comparison.

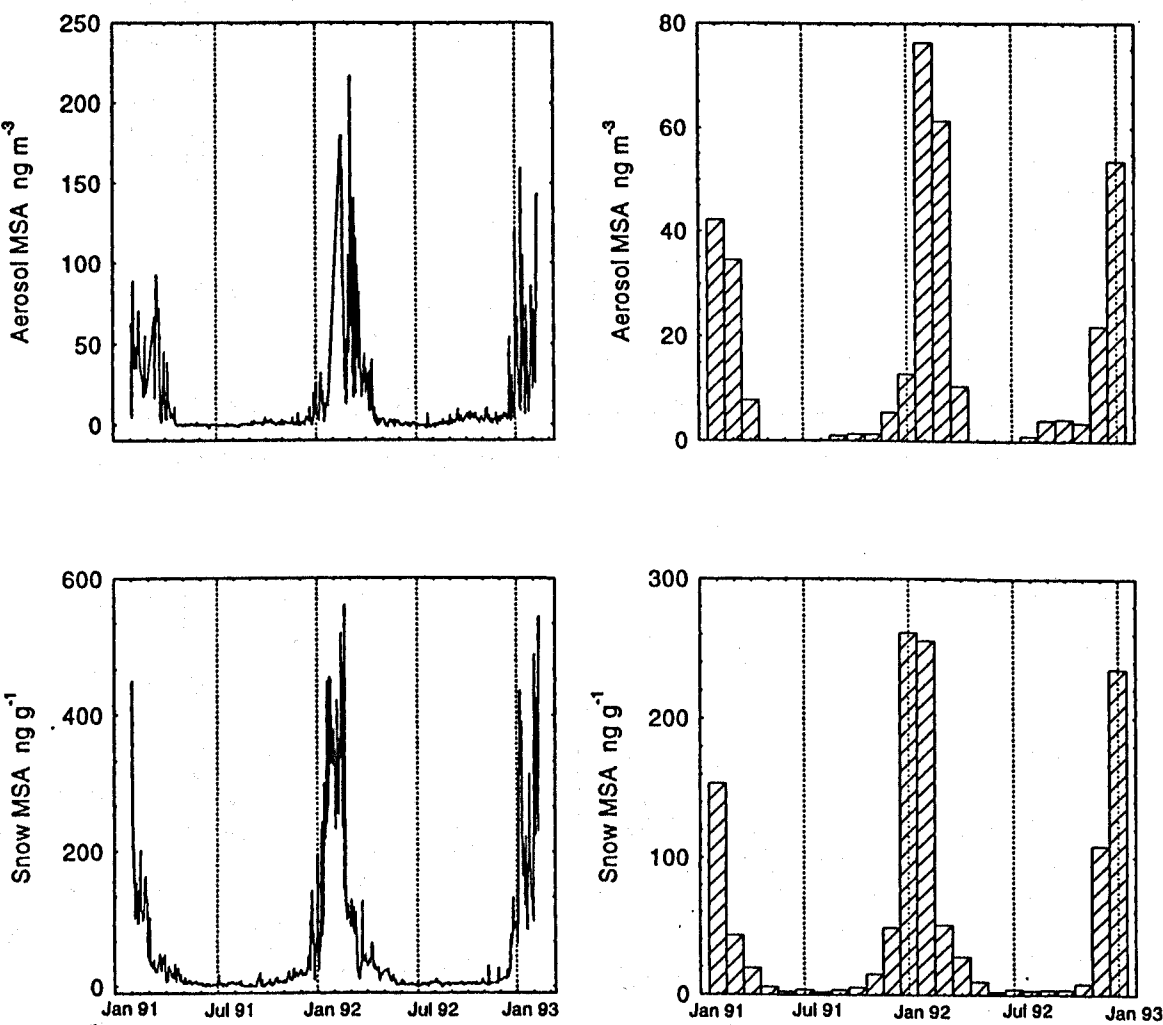


Figure 4.10: Episodes of high MSA loadings in daily the aerosol (dashed line and squares) and snow (solid line and triangles) record at Halley, looking at specific days in the time series.

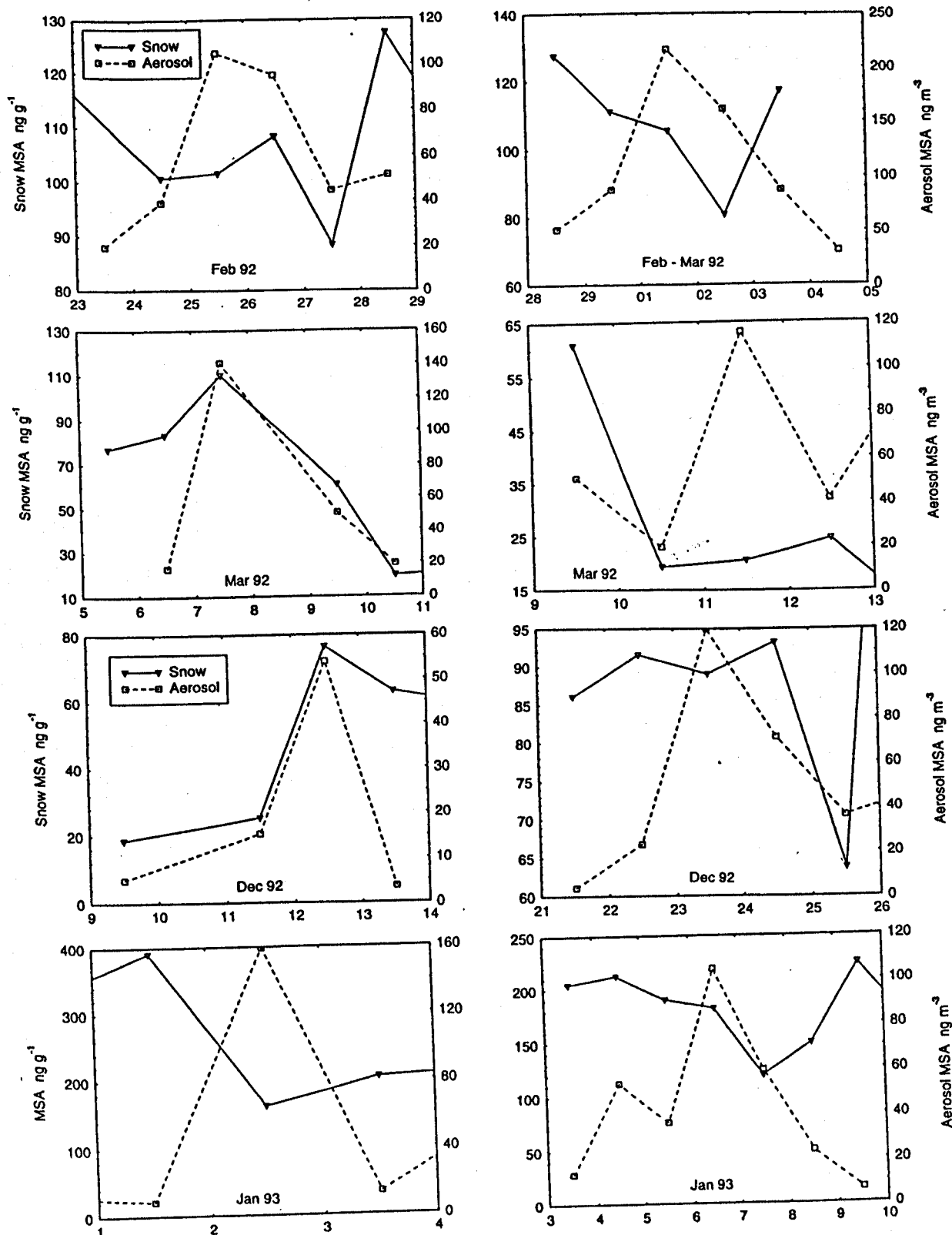


Figure 4.11: Closer examinations of daily aerosol (dashed line and squares) and snow (solid line and triangles) MSA concentrations at Halley, looking at specific months in the time series.

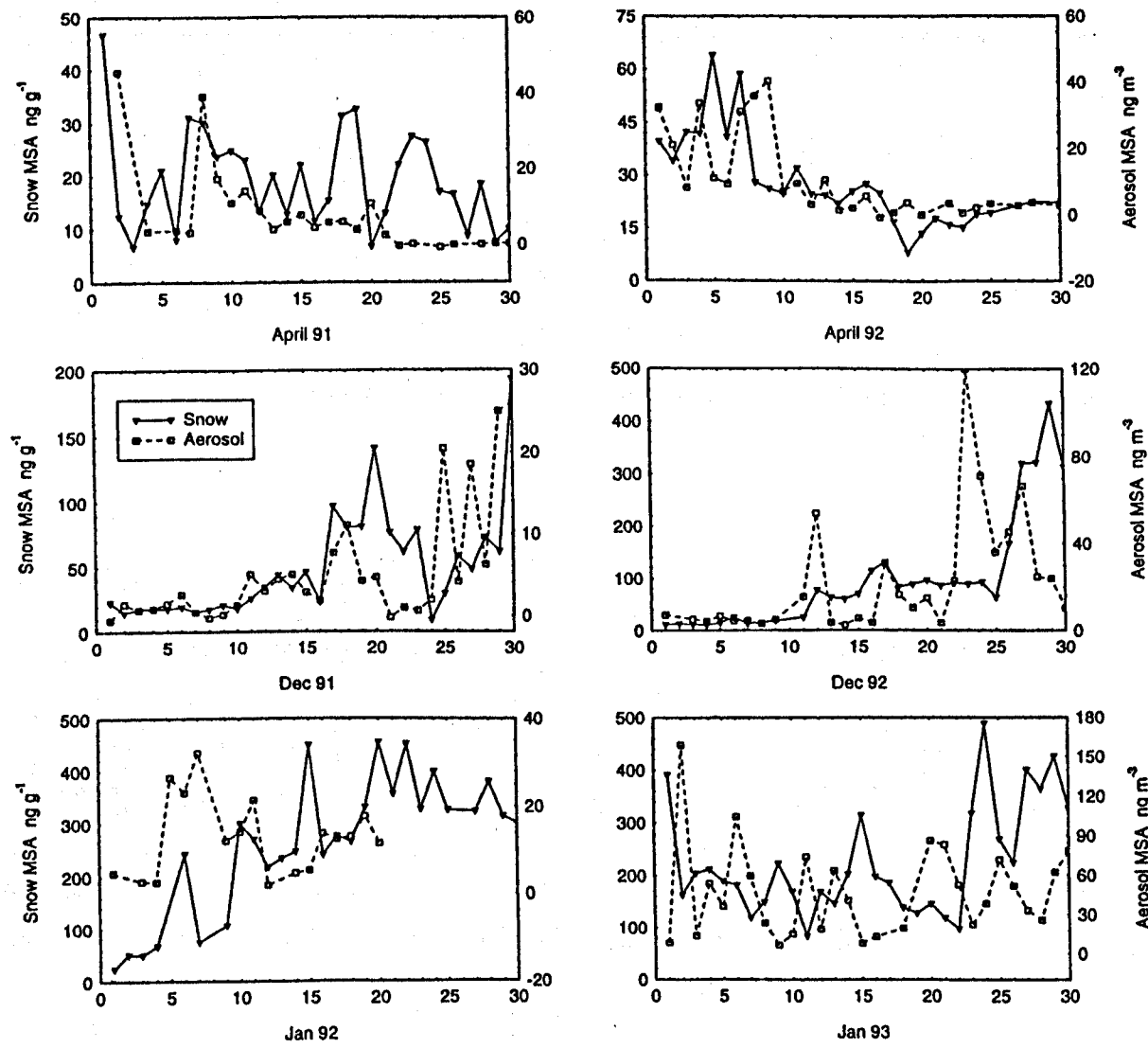


Figure 4.12: Individual events of the highest snow (solid line and triangles) MSA variability and the corresponding aerosol (dashed line and squares) concentrations for those days.

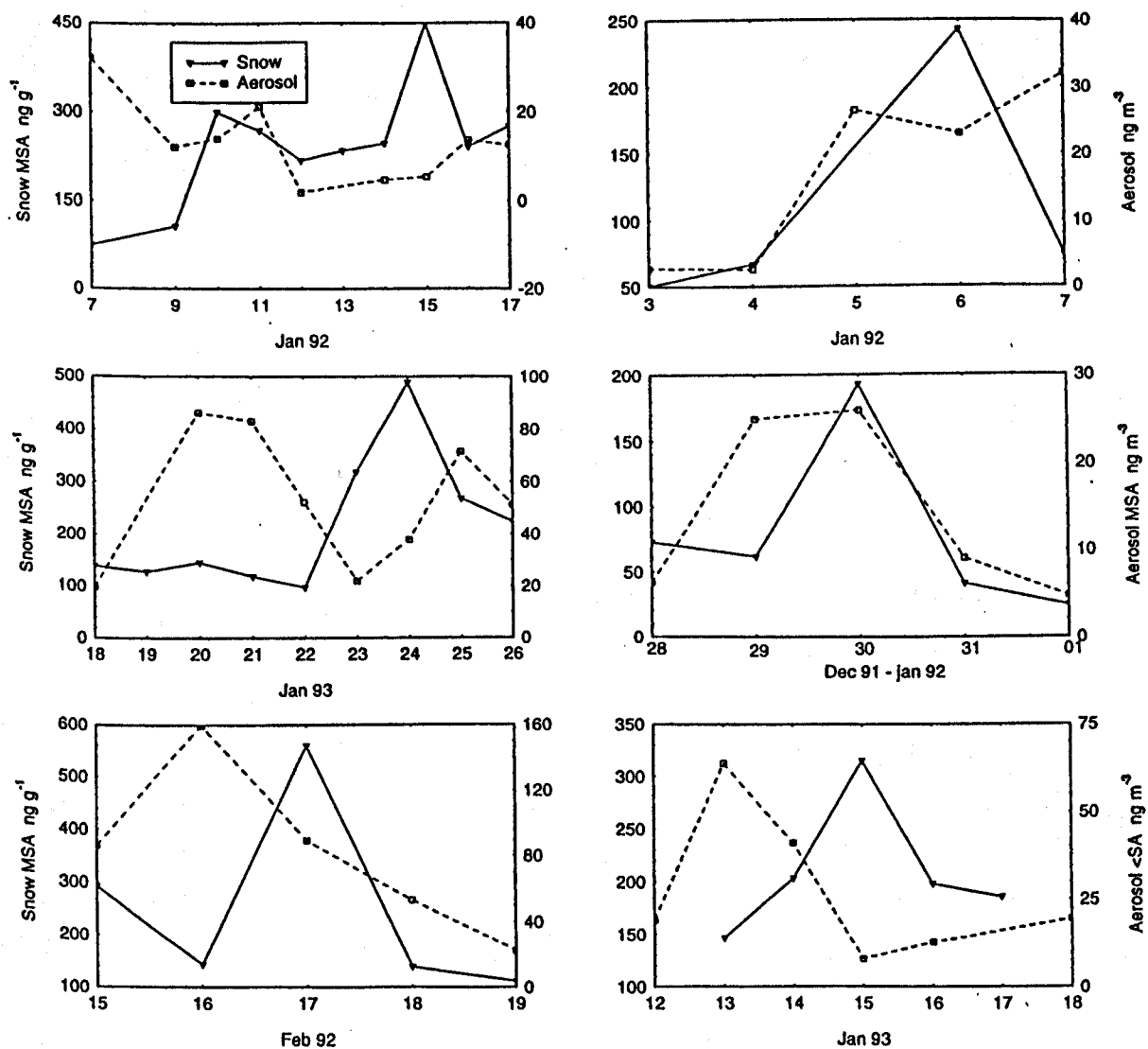


Figure 4.13: Halley snow samples, *s1* (collected from the upper 10 mm of snow) and *s2* (collected from below this, between 3-15 mm), plotted against one another for sea salt, MSA and corrected nss sulphate (calculated using BSW ratio = 0.073).

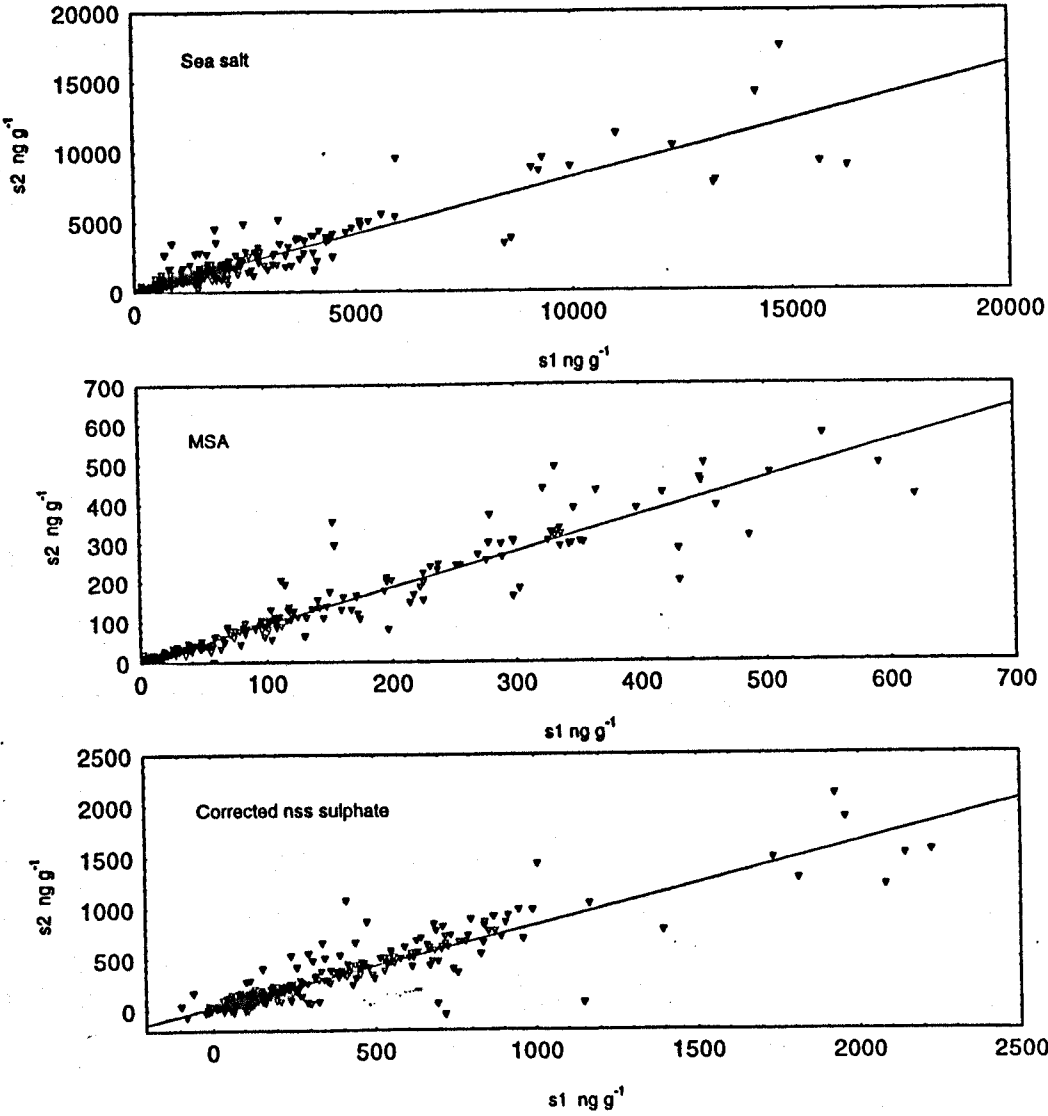
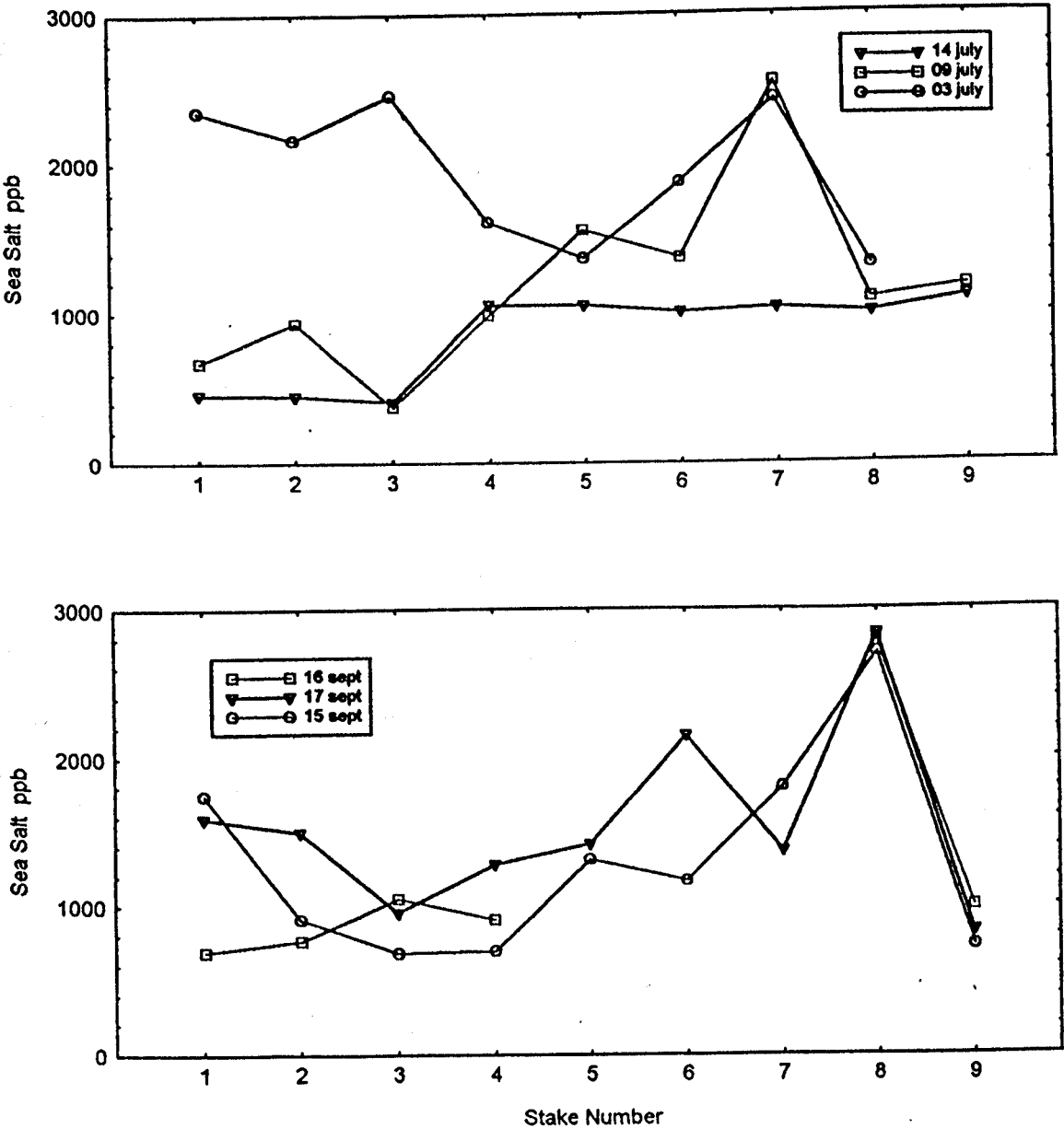


Figure 4.14: Sea salt concentration in surface snow, after three events of drift, at each of the nine stakes. The upper plot shows three events in July 1993 and the bottom plot three events in September 1993.



Chapter 5

Aerosol Deposition Processes in Antarctica

5.1 Introduction

This chapter will look at the various deposition processes that remove chemical species from the Antarctic atmosphere and deposit them in the snow. The chapter expands upon ideas from a paper by Wolff & Hall et al., [in press]. The processes of dry deposition, wet deposition, wind pumping, sublimation, drifting and blowing snow and fog deposition will be examined individually. The relationship between aerosol concentrations and chemical concentrations in fresh and aged snow from Halley is quantified. Theoretical models will be compared with the experimental data and the velocity of deposition calculated and used to determine deposition fluxes. The relative contribution and importance of each process is estimated, in an attempt to better understand the concentrations finally seen in snow, and ultimately in coastal Antarctic ice. The dominant deposition process is identified and the controlling factors which determine this, are also discussed.

5.2 The Air-Snow Transfer Function

Air-snow transfer of aerosol species is a complex process, dependent not only on the concentration of particles in the atmosphere, but on specific processes of the snow and air. The transport of aerosols from the air to the snow surface, can best be described in terms of a flux, defined as the amount of chemical species deposited to a surface per unit time, per unit area. The commonly used air-snow transfer function is:

Equation (5.1)

$$F_T = V_d C_{air} + \rho_w P C_{snow}$$

where:

F_T = total flux ($\text{ng m}^{-2} \text{s}^{-1}$)

V_d = dry deposition velocity (m s^{-1}),

C_{air} = concentration in air (ng m^{-3}),

ρ_w = the density of snow meltwater (1000 kg m^{-3}),

P = snow precipitation rate (metres water equivalent s^{-1}) and

C_{snow} = the chemical concentration in snow (ng kg^{-1}).

Simply, the total flux is comprised of the dry and wet deposition fluxes. In a more complex model, other deposition processes such as wind pumping, sublimation, drifting and blowing snow and episodes of fog, also need consideration. In order to quantify this more detailed air-snow transfer function, all of the individual components must be determined.

5.3 Dry Deposition Process

Dry deposition is the continuous process of aerosol and gas transport from the atmosphere, to a surface, occurring in the absence of precipitation [Davidson, 1989]. Particle transport,

through dry deposition, is considered to occur in three stages. Initially, particles move from the lowest levels of the atmosphere, a few tens of metres above the surface, into the molecular boundary layer, located less than 1 mm above the surface [White et al., 1989]. This first stage is known as **aerodynamic transport** [Davison, 1989] and occurs either by eddy diffusion, or sedimentation processes. Eddy diffusion causes particles or gases to move as a result of turbulent wind eddies, from areas of high, to low concentration. The sedimentation mechanism is the gravitational settling of particles [Cunningham & Waddington, 1993] and is dependent on particle size, shape and density [Davidson, 1989].

The second stage is known as **boundary layer transport**, and moves air and contaminants across the molecular sub-layer to the snow surface. This can occur by four mechanisms; diffusion, interception, inertial motion and sedimentation [Davidson, 1989]. Transport by diffusion results from either the movement of air eddies, or Brownian motion, whereby particles move down a concentration gradient, due to the random thermal energy they possess. Interception occurs when particle size is greater than the sub-layer height. Particles will then collide with the surface, particularly with protruding, irregularly shaped ice crystals. Inertial deposition involves two mechanisms; inertial impaction and turbulent inertial deposition. Impaction occurs when particles cannot follow rapid changes in the direction of the mean air flow, and their inertial energy carries them across the sub-layer, to the surface. Inertial deposition is the result of air eddies carrying particles across the sub-layer, again by inertial energy.

The final stage in the dry deposition process is **surface interactions**, in which contaminants adhere to the surface. It is this stage that determines whether particles attach to snow irreversibly, or are later re-emitted.

The significance of dry deposition to the chemical concentrations found in snow and ice, in polar regions, is uncertain. In areas where snow accumulation rates are very low ($<50 \text{ kg m}^{-2} \text{ yr}^{-1}$), such as central Antarctica, dry deposition is thought to be the dominant deposition process [Pourchet et al., 1983]. However, at Dye 3, Greenland [Davidson et al., 1993] and Summit, Greenland [Bergin et al., 1995], where snow accumulation is greater ($500 \text{ kg m}^{-2} \text{ yr}^{-1}$ and $210 \text{ kg m}^{-2} \text{ yr}^{-1}$ respectively) dry deposition plays only a small role. It is important to clarify the significance of the dry deposition process and this study attempts to do this, both experimentally and theoretically, for coastal Antarctica.

5.3.a Calculation of the Dry Deposition Flux

The process of dry deposition can be described in terms of a deposition rate, per unit area, for a chemical species to the snow. This is known as the dry deposition flux and can be expressed as:

Equation (5.2)

$$F_d = V_d C_{\text{air}}$$

where:

F_d = the dry deposition flux ($\text{ng m}^{-2} \text{ s}^{-1}$),

V_d = dry deposition velocity (m s^{-1}) and

C_{air} = the concentration in air (ng m^{-3}), as a function of height above the surface [Davidson, 1989].

Values for C_{air} are taken from existing aerosol records, and are readily available from the daily Halley data set. Dry deposition velocities (V_d) can either be estimated theoretically, using model predictions, or experimentally.

5.4 Experimental Estimates of Dry Deposition

As dry deposition is the transfer of chemical species to the surface in the absence of precipitation, dry deposition fluxes can be determined by comparing snow concentrations over a period of days, when no snowfall (or drift) occurred. Using this experimentally determined dry deposition flux (F_d), known aerosol concentrations (C_{air}) and equation 5.2, the dry deposition velocity can be calculated. Three experimental approaches can be taken in determining V_d .

5.4.a Method One

Periods of days when no significant snowfall (or drift) occurred at the sampling site can be identified by monitoring the level of snow at a stake, located at this site. Simply, any events of precipitation should be indicated by an increase in snow level at the stake (Figure 5.1).

Events were selected if the accumulation at the snow stake was less than 0.5 cm and remained less than this for at least four days. The events that fit this criterion for sea salt

and MSA are shown in figures 5.2 and 5.3 respectively. However, using this method for estimating the chemical flux, presents us with some problems. Both sea salt and MSA show significant variability during an event, when no apparent accumulation occurred at the stake. These fluctuations are often very large, of the order factor 15 in some cases (eg. mid June 1991 and end February 1993, in figure 5.2), and are unlikely to be due to dry deposition alone.

There are two likely causes for these fluctuations. Firstly, spatial variability, due to drifting snow during the 4-day episodes, will cause different ages of snow to be sampled, even over the scale of a few cm (see section 4.10, spatial variability). Secondly, there are a number of small precipitation events that are not recorded at the accumulation stake. Although measurements at the snow stake indicated that little, or no accumulation occurred on the days shown in figures 5.2 and 5.3, the detailed 3 hourly meteorological record does document instances of precipitation on many of these days. This was either in the form of snowfall, fog, drifting or blowing snow. One or more of these precipitation events (an event implies a precipitation code was recorded in a 3-hourly meteorological reading), occurred on 615 days out of the 2 years (Table 5.1). We can conclude that accumulation measurements at a single stake cannot alone show whether a surface is unchanging, and precipitation records should also be monitored, particularly to identify days when drifting and blowing snow occurred.

Table 5.1: The occurrence of precipitation over the 2 year time period of this project, at Halley.

Precipitation type	No. of events	No. of days
Drifting snow	724	131
Blowing snow	359	44
Snowfall	1161	378
Fog	405	183

5.4.b Method Two

The criterion for selecting days when dry deposition could occur can be narrowed in an attempt to overcome the problem of patchy snow deposition. Instead of basing accumulation solely on the snow stake measurements, 3-hourly meteorological data can be used as well, to identify days when no reports of snowfall, drift, blowing snow or fog were recorded. Over the 2 years, there were 141 such days. This is reduced to just 9 events if a sequence of at least 3 days of no accumulation follows, or 18 events if only 2 days are required. The number of suitable days is even further reduced if the snow stake accumulation record is also taken into account. Inclusion of this information results in only 5 events, lasting for no more than 2 days each, meeting the criterion.

For these limited number of events, the concentration variability between days, in the surface snow, was slightly less, as to be expected for a shorter time period. However, concentrations for all ions (sea salt, MSA and nss sulphate) still fluctuated widely, with decreases as well as increases, as seen in figure 5.4. More events are needed to confidently

use these two methods for determining the dry deposition flux.

5.4.c Method Three

An alternative approach to calculate the dry deposition flux is needed, which takes into account patchy snow concentrations, due to drifting snow and provides a larger data set than method 2. Suitable events were therefore chosen if the concentration of the chemical species in surface snow, over a period of a few days, changed very little and on these days, no significant accumulation occurred at the stake. This method assumes that dry deposition is a gradually occurring processes and would not cause a huge step in the snow concentration from day to day.

Events were selected if the daily change in surface snow concentration was less than 100 ng g⁻¹ and the accumulation, measured at the snow stake, was less than 0.5 cm. Only 24 suitable events were found, and these occasionally lasted for only 2 days. For these 24 events, the V_d can be found from the gradient of daily concentration changes in surface snow, plotted against aerosol concentration for the same 24 hours (Figure 5.5). This gives a dry deposition velocity of 0.35 ± 0.2 cm s⁻¹. However, the scatter for individual daily values is considerable. Removal of just a few outlying points significantly alters the gradient and therefore limits the accuracy of the result.

This value compares with dry deposition velocities determined from impactor data

(measuring aerosol mass size) and snow deposition theory (see section 5.5), by Bergin et al., [1995] for Summit, Greenland, who found V_d for sea salt particles between 0.064 cm s^{-1} - 0.11 cm s^{-1} .

5.4.d Conclusion

Any site where significant spatial variability exists, renders experimental determination of dry deposition extremely difficult. Despite daily sampling at Halley, it is hard to find days when the surface concentrations remain stable for long periods of time. One solution to this problem may be to use surrogate surfaces to capture dry deposition on a stable medium. Teflon sheets have been successfully used at Summit, Greenland to do this [Bergin et al., 1995]. They have the advantage of ensuring that the same surface is stable for long periods of time. Bergin et al., [1995] found that dry deposition velocities determined from Teflon sheets were comparable with those determined by impactor size measurements and snow deposition models. For sulphate he found $V_{d(\text{impactor})}$ gave $0.021 \text{ cm s}^{-1} \pm 0.024 \text{ cm s}^{-1}$, and $V_{d(\text{Teflon})}$ gave $0.041 \text{ cm s}^{-1} \pm 0.021 \text{ cm s}^{-1}$. However, this approach may give differing results, depending on the surrogate surface used and dry deposition velocities determined on Teflon sheets may not be accurate for a surface of snow. Further study of this method is therefore required.

5.5 Model Estimates of Dry Deposition

Dry deposition velocities can also be calculated theoretically, using mathematical models. They provide a particle size dependent value of V_d . Traditionally, most models were developed for vegetated surfaces, however, a few calculations do concentrate on deposition to a snow surface.

A simple model, using bulk chemical analysis and scanning electron microscopy of aerosol and snow samples collected simultaneously, was used by Dick [1990] to determine dry deposition velocities for 3 different aerosol size modes in coastal Antarctica. For the small mode, with particles of diameter $0.3 \mu\text{m}$, the model predicted dry deposition velocities of 0.002 cm s^{-1} . For the large mode (particle diameter $2 \mu\text{m}$), V_d was 0.14 cm s^{-1} and 5.0 cm s^{-1} for the coarse mode (particle diameter $20 \mu\text{m}$).

Ibrahim et al., [1983] proposed a more complex model to take into account the individual mechanisms of dry deposition onto snow, such as boundary layer transport, and surface interactions. Using this approach, the dry deposition velocity (V_d) is quantified in terms of resistance to transport. Further discussions on the calculation of depositional resistance can be found in Davidson et al., [1989].

Davidson, [1989] applied the Ibrahim et al., [1983] model to conditions found at Dye 3, Greenland, during summer 1980. Figure 5.6 shows the model results, with dry deposition

velocities plotted against the logarithm particle diameter. The model assumes a roughness height (z_0) of 0.007 cm. (The z_0 value is a mathematical term, representing the y-intercept on a plot of wind speed versus the logarithm of height (y-axis) [Davidson, 1989]). An average friction velocity of 9.1 cm s^{-1} is also used, and this term relates to wind shear stress at the surface of Dye 3, during summer 1980. The model also assumes a stable atmosphere, at 0% humidity. Using a relative humidity closer to that generally found at Halley (93%) would increase the deposition velocity.

Direct use of the model, for conditions at Halley, is not possible, as aerosol size distribution studies have yet to be undertaken. However, initial values for the dry deposition velocity can be obtained by estimating the particle sizes expected. For sea salt, which represents a largely local source (see chapter 3), the majority of particles (number concentration) are likely to be a few microns in diameter. Applying this approximated particle size to the model results in figure 5.6, dry deposition velocities for the majority of sea salt will be of the order 0.2 cm s^{-1} . This confirms the work by Dick, [1990] who found for particles of diameter $2 \mu\text{m}$, V_d was 0.14 cm s^{-1} .

Sea salt particles can also exist as giant particles, with diameters of $10 \mu\text{m}$ or more. These very large particles could have deposition velocities of as much as a few cm s^{-1} , due to sedimentation processes, as shown by Dick's work (diameter $20 \mu\text{m}$, $V_d = 5 \text{ cm s}^{-1}$). Also, the previously determined experimental upper limit of 0.55 cm s^{-1} (section 5.4.c) is unlikely to include really large episodic inputs of sea salt, as our aerosol sampler may not have been

able to collect giant particles (see section 3.3). However, this may not be a problem, as it is likely that drifting and blowing snow, rather than dry deposition, is the final removal mechanism from the atmosphere, for these very large particles.

For MSA and non sea salt sulphate, particle sizes will range from 0.1-1 μm (see section 3.8a), representing the longer source range for these species. Dry deposition velocities for these species (using figure 5.6), will therefore be of the order 0.04 cm s^{-1} .

5.5.a The Annual Dry Deposition Flux

Having obtained model estimates for the dry deposition velocities, it is possible to calculate a value for the dry deposition flux for individual chemical species at Halley. The average yearly flux is determined by multiplying V_d by the mean aerosol concentration (C_{air}) over a year (equation 5.2). For sea salt, C_{air} is 162 ng m^{-3} , for MSA 15 ng m^{-3} and for non sea salt sulphate 49 ng m^{-3} . The annual dry deposition fluxes, calculated using the theoretical model of Davidson, [1989] and experimental dry deposition velocities (determined by method 3, section 5.4.c), are shown in table 5.2. Experimental values are quoted as upper limits because it is difficult to exclude all other deposition processes from this flux value.

Table 5.2: Estimates of the annual dry deposition flux at Halley, during 1991 and 1992.

¹ The dry deposition fluxes for sea salt, do not include giant particles.

Species	Annual Dry Deposition Flux ($\text{ng cm}^{-2}\text{yr}^{-1}$)	
	Experimental Limit	Theoretical Estimate
sea salt ¹	<3060	1020
MSA	<280	20
nss sulphate	<870	60

In conclusion, the process of dry deposition, when compared to the **total flux** (see section 5.11) to the surface (see tables 5.9 & 5.10), makes a minor contribution to the fluxes of chemical species to the snow surface at Halley. Giant sea salt particles, however, will rely on this process to a greater extent and could make a more significant contribution to the sea salt snow budget. Also, at Halley, particle size distribution studies are needed to accurately account for the dry deposition process.

5.6 Wind Pumping Process

Wind pumping is the filtering of air by snow, and can occur through any undulating porous surface. It is likely to have the effect of increasing snow concentrations. Simply, dirty air enters a snow pack, depositing aerosols as it passes through, and clean air leaves. As wind passes over the snow surface, any undulations in the microtopography will create areas of high and low air pressure [Colbeck, 1989]. The resulting pressure gradients will force air through the snow pack. The continual action of air moving in and out of snow, greatly increases the surface area available for deposition. It is estimated that for a square cm of snow, ventilated to a depth of 1 cm, the surface area increases by a factor 100 [Harder, 1996].

The bumpy surface required for wind pumping to occur, is primarily the result of wind erosion and deposition of snow [Cunningham & Waddington, 1993]. Common depositional features include barchans, dunes and ripples and common erosional features

are sastrugi and erosion pits [Harder, 1996]. However, in practice it is often difficult to distinguish between these different forms of microtopography, with authors tending to refer to sastrugi as an all-inclusive term.

It is thought that air passing through sastrugi will deposit aerosol material in the nose of the sastrugi (the face which the prevailing wind direction hits first, (see figure 2.8)), resulting in elevated concentrations, in comparison with the tail, where filtered air leaves [Waddington, 1996].

The frequency of sastrugi occurrence and their size and shape, has not been systematically studied, only broad descriptive comments made. Kotylakov [1966] states that almost the entire surface of the Antarctic continent is covered with sastrugi and Kruchinin [1965] estimated that sastrugi covered 90-95% of the total surface area of the Lazarev Ice Shelf, during the winter. Gow [1965] describes the surface microtopography of South Pole in more detail, describing the annual cycle of sastrugi formation and migration. Harder [1996] also comments that sastrugi are common at South Pole, and follows this up with chemical investigation of their composition. She examines two sastrugi in detail, and finds that sulphate concentrations are as much as $4\frac{1}{2}$ times greater in the nose, than the tail. This supports the theory that significant wind pumping occurs through the sastrugi and acts to concentrate chemical species. However, sublimation could also be a factor in achieving an elevated concentration and the relative humidity must be known at the time of sampling. A high humidity, with continual movement of air across the boundary sub-layer, is not

likely to cause sublimation.

The wind pumping processes is difficult to quantify. Its effects are not taken into account by dry deposition models [Davidson et al., 1996], and it cannot be distinguished from dry deposition, in experimental data. Specific models and field studies for wind pumping deposition are therefore required.

5.6.a Experimental Estimates of Wind Pumping

To investigate further the theory that sastrugi act as filters for aerosol particles, a small scale study was undertaken at Halley research station, in summer 1995. Six sastrugi were sampled, with collections taken from three places, and in 3-dimensions, from the feature and notes on the surrounding topography were also made [see section 2.11.b, for information on sastrugi sampling techniques]. The average relative humidity on the day of collection was 93%.

The expected pattern of significantly increased concentration in the sastrugi nose, compared with the tail was not seen (Figure 5.7). The nose tended to be just 10% more concentrated than the tail. This very small percentage difference between the concentrations in the sastrugi nose and tail indicates that neither wind pumping, nor sublimation, affected the microtopographic features at Halley. This may be because the sastrugi were sampled soon after formation (1 day) and were not sufficiently aged to show the effects of wind pumping.

To check this hypothesis, the same sastrugi formation would need to be sampled over a period of days. However, in areas such as the Brunt Ice Shelf, where Halley is located, sastrugi are fairly scarce, making continued monitoring a difficult task. Even after severe blowing snow conditions sastrugi features may not be present.

Typical features that do exist at Halley consist of a collection of large sastrugi, (although these features are a lot smaller compared with those reported from the Antarctic Plateau [Harder, 1996]), with heights of the order 10-30 cm and wavelengths 2-10 m, surrounded by much smaller features, of only 2 cm high and 10 cm in wavelength. These smaller features tend to have hard, icy surfaces, making them less susceptible to wind pumping.

Table 5.3 shows the measurements of 8 randomly selected sastrugi at Halley.

Table 5.3: Measurements of sastrugi at Halley, during summer 1995.

Feature	Height (cm)	Length (m)	Width (cm)
1	13	0.38	16
2	22	1	80
3	12	10	22
4	12	0.80	50
5	7	0.95	30
6	25	1.5	50
7	1	12.6	430
8	2	7	30

5.6.b Theoretical Estimates of Wind Pumping

If we assume that the lack of experimental evidence for wind pumping at Halley, is due to the immaturity of the features sampled and that, given time, wind pumping would alter the concentration of the snow, we still need to account for the contribution this process makes to the total flux at Halley.

The wind pumping deposition velocity can be estimated using a model by Waddington [1996]. The model parameters are based around the topographic features of the sastrugi at a certain wind speed. The equation is given as:

Equation (5.3)

$$V_w = \frac{k}{\mu} \frac{6\rho_{air}U_{10}^2}{\pi} \frac{h}{\lambda} \frac{1}{\lambda} \frac{\sqrt{\alpha^2+1}}{\alpha}$$

where:

V_w = wind pumping deposition velocity (ms^{-1})

k = snow permeability ($4 \times 10^{-9} \text{ m}^2$)

μ = viscosity of air ($1.6 \times 10^{-5} \text{ Pa}$)

ρ_{air} = density of air (1 kgm^{-3})

U_{10} = wind speed at 10m above surface (6 ms^{-1} - average)

h = sastrugi height

λ = distance between each sastrugi feature

α = horizontal aspect ratio (0.5)

For typical sastrugi features at Halley ($h = 0.2 \text{ m}$, $\lambda = 4 \text{ m}$), the calculated deposition velocity is 0.04 cm s^{-1} and increases to 2 cm s^{-1} for smaller features with $h = 0.02 \text{ m}$ and $\lambda = 0.2 \text{ m}$. However, the impermeable nature of the smaller sastrugi, due to their hard, icy

faces, makes a deposition velocity of 0.04 cm s^{-1} seem more realistic. Also, sastrugi at Halley are often quite rare and at any give moment only cover a small percentage of the surface, so the effective deposition velocity is likely to be well below 0.04 cm s^{-1} .

The wind pumping deposition flux at Halley can be estimated using equation 5.2 and the average aerosol concentrations (C_{air} sea salt 162 ng m^{-3} , nss sulphate 49 ng m^{-3} , MSA 15 ng m^{-3}), (Table 5.4).

Table 5.4: Estimates of the annual wind pumping deposition flux at Halley, during 1991 and 1992.

Species	Annual Wind Pumping Deposition Flux ($\text{ng cm}^{-2}\text{yr}^{-1}$)
	Theoretical Estimate
sea salt	<200
MSA	<20
nss sulphate	<60

The wind pumping process is negligible in comparison to the other processes examined in this study. However, at locations where snow accumulation rates are lower and larger, and more stable sastrugi are present (such as South Pole), this may be a more important process.

5.7 Sublimation Process

Sublimation from the snow surface, or stationary sublimation, is also likely to cause an increase in surface snow chemical concentrations. This can be misinterpreted as dry deposition in experimental studies. One way of detecting sublimation is to observe small

reductions in the surface level at a snow stake. At Halley, the largest number of small reductions ($<1\text{cm}$) are found during November-February, a time period when sublimation is most likely to occur.

Stationary sublimation (rather than sublimation that is associated with blowing and drifting snow - see later), amounts to 4.22 mm water equivalent during winter at Halley [King et al., 1996]. The average annual accumulation at Halley is 324 mm water equivalent [King et al., 1996], and this means that sublimation, in this part of the year, contributes 1.3% to the total annual water budget, and is unlikely to have significant effect on snow concentrations.

Estimates of the sublimation rate during summer, are still uncertain, but could range between 30 and 70 mm water equivalent [Limbert, 1963], or 1 mm water equivalent per day [King et al., 1996]. Over a year, this gives a contribution of between 9 and 20%. To be confident on the importance of this process, a better estimate for summer sublimation rates is required.

5.8 Wet Deposition Process

Wet deposition is the removal of aerosol particles and gases from the atmosphere by precipitation. There are generally thought to be 3 categories of precipitation scavenging. These are nucleation, in-cloud and below-cloud scavenging. Theoretical discussions on wet

deposition can be found in Barrie, [1992]; Davidson, [1991; 1989] and Pruppacher & Klett, [1980].

Nucleation scavenging occurs when ocean borne particles such as sea salt and non sea salt sulphate, act as condensation nuclei, which water vapour can then condense upon. The resulting droplets are carried in-land by the prevailing winds, and rise with the elevation of the ice sheet. The droplets continue to grow to sizes of 100 μm or more, by diffusion of water vapour. The particle nucleus is then removed from the atmosphere during a snowfall event.

Once the aerosol particles have become active as nuclei, the ice crystals and water droplets can aggregate to form snowflakes. Some of the remaining liquid droplets also collide with the ice crystals and snowflakes, freezing on contact. This results in the formation of rime, and will be discussed later in section 5.10.

In-cloud scavenging occurs as contaminant particles and gases collide with cloud water, snowflakes or raindrops. For collisions to occur, winds must move through the clouds and the aerosol particles must cross a viscous sub-layer that surrounds each snowflake and raindrop. The same transport mechanisms described earlier for dry deposition, such as aerodynamic and boundary layer transport, are relevant here, as movement across the sub-layer occurs by the same means.

As with in-cloud components (liquid droplets, ice crystals, raindrops and snowflakes), **below-cloud scavenging** by falling snow and rain, can also collect particles during a precipitation event. The same transport steps as in-cloud scavenging and dry deposition are again important here, as once more there is a viscous sub-layer around each snowflake and raindrop, which the aerosol particle must cross.

5.8.a Calculation of the Wet Deposition Flux

An expression for the flux of chemical species with snowfall can be written, which takes into account the chemicals contained within snow. The special case of fog and rime, whereby cloud droplets do reach the snow surface, is discussed in section 5.10. A wet deposition flux can be expressed as:

Equation (5.4)

$$F_w = \rho_w P C_{\text{snow}}$$

where:

F_w = the wet flux ($\text{ng m}^{-2} \text{s}^{-1}$),

ρ_w = the density of snow meltwater (1000 kg m^{-3}),

P = the snow precipitation rate (m water equivalent s^{-1}) and

C_{snow} = the chemical concentration in snow (ng kg^{-1}).

5.8.b Scavenging Ratios

Accounting for the various mechanisms that determine the snow concentration (C_{snow}) is difficult. One approach is to define a scavenging ratio, empirically relating the chemical

concentration in the snow to the concentration in the air. This can be written as:

Equation (5.5)

$$W = \frac{\rho_{air} C_{snow}}{C_{air}}$$

where:

W = the dimensionless mass scavenging ratio,

ρ_{air} = the density of air (1 kg m^{-3}),

C_{snow} = the snow concentration (ng kg^{-1}) and

C_{air} = the aerosol concentration (ng m^{-3}).

The scavenging ratio can be estimated empirically for individual snowfalls, provided fresh snow is collected after a snowfall event. Collections of fresh snowfall were made at Halley, when the snow surface increased by 1.5 cm, measured at a snow accumulation stake. (More detailed information on accumulated snow collection can be found in section 2.9.b(ii)). In most cases, several samples (up to 12) of accumulated snow were collected following a snowfall event. For the purposes of determining a scavenging ratio, these concentrations have been averaged to obtain a single concentration for a snowfall. In total, there are 50 snowfalls, corresponding to 342 samples. The scavenging ratios can be determined in two ways.

5.8.b(i) Method One

Firstly, plotting accumulated (or fresh) snow concentration against aerosol concentration, gives the scavenging ratio (actual gradient is W/ρ , but as ρ is taken as 1, then term becomes W) as the gradient of the best fit line (Equation 5.5). The aerosol concentration used is from the 24 hours preceding the snowfall.

For MSA and nss sulphate, there is a weakly significant correlation between snow and aerosol concentrations, $r^2 = 0.39$ and 0.5 respectively (Figure 5.8). The correlation is stronger for these species than sea salt, but this may simply reflect the stronger seasonal cycle that MSA and nss sulphate possess in both snow and air. For all species there is considerable scatter amongst the data and this is can be seen in the large gradient error (Table 5.5). The correlation for sea salt is not statistically significant, $r^2 = 0.002$.

5.8.b(ii) Method Two

Scavenging ratios can also be determined individually (using equation 5.5) for each relevant day in the Halley data set. Average (geometric means) W values can then be calculated for the time period (Table 5.5). For this determination, only aerosol and snow concentrations above the detection limit (see tables 2.5 and 2.7) are used.

The large differences between the W values determined by regression and geometric means, highlights the extreme uncertainty of the numbers obtained here.

5.8.b(iii) The Significance of Scavenging Ratios

There is a surprising lack of W values in the literature and this makes it difficult to comment on the representability of the values determined at Halley. Other reported scavenging ratios from Antarctica and Greenland are shown in table 5.5.

Table 5.5: Other reported scavenging ratios (W) for Antarctica, Greenland and North America.

W	Sea Salt	MSA	nss Sulphate
Halley (Regression)	120±340	630±280	910±140
Halley (Average)	11060	6540	4800
Dumont D'Urville [Wolff et al., in press]	----	1586	----
Neumayer [Wolff et al., in press]	5781	792	958
Antarctic Peninsula [Dick & Peel, 1985]	7795±3898	----	----
Dye 3, Greenland [Davison et al., 1985]	6497±3898	----	180±120
Summit, Greenland [Davidson et al., 1985]	----	----	220±129

In general, it can be said that $W_{\text{sea salt}}$ values are greater than W_{MSA} and $W_{\text{nss sulphate}}$. These higher ratios may be due to more efficient removal of sea salt. Sea salt particles generally tend to be larger than MSA and nss sulphate and may therefore result in more efficient scavenging. Also, the very local nature of the sea salt source (see chapter 3) may also result in a greater number of giant particles being present.

Other differences in the data are that values for non sea salt sulphate in Greenland, seem to be less than those found at other Antarctic locations. There are also considerable differences for each species between all sites. This could simply be due to the different sampling techniques employed. Halley is the only Antarctic site where daily aerosol collections were made. At Dumont D'Urville, accumulated snow concentrations are

matched with aerosol concentrations that cover a 4-7 day period. At Neumayer, aerosol sampling lasts for between 1 and 2 weeks. It is conceivable that longer aerosol sampling dilutes the significance of the aerosol values. Consequently, the value obtained is not representative of the chemical concentration on a daily basis, and certainly not representative of the air just before a precipitation event. The scavenging ratios for the Antarctic Peninsula are based on just 5 summer snowfalls [Dick & Peel, 1985], and 3 and 8 snowfalls at Dye 3 and Summit, Greenland, respectively. The lower W values obtained here may be due to the short sampling campaign and restriction to summer snowfalls.

A second sampling difference is that Halley aerosol collections were made at 2 m above the surface and other stations, such as Neumayer, sample at a higher altitude. It is possible that sideward drift of snow cleanses the air, before it is actually sampled on the filter faces at Halley. At Neumayer, the station closest to Halley base, the filter intake tube is approximately 7 metres above the surface. At this height the influence of drifting snow, which occurs generally below eye level, may be less important. Presumably at greater elevations the air would rarely come into contact with drifting snow and would not be filtered, or cleansed to the same degree. If this is indeed the case, scavenging ratios determined from aerosol concentrations at ground level, would be greater than those from aerosol sampling sites collected at higher levels.

Thirdly, it is impossible to be sure that the Halley accumulated snow samples are 100% fresh snow. At stations such as Dumont D'Urville and Neumayer, accumulated snow

samples are only collected if the wind speed is low and no drifting or blowing snow is observed. At Halley, since it nearly always drifts when it snows, this distinction was not possible. Instead samples are collected when there is a significant increase at the snow accumulation stake, regardless of the weather. If the snow samples from Halley are not fresh snow, they may contain impurities from a previous snowfall event.

With these problems in mind, it can be concluded that scavenging ratios are not a valid method for commenting on wet deposition and an alternative approach to determine wet deposition is needed. Until a standard sampling protocol is established this will continue to be a problem.

5.8.c Accumulated Snow

Wet deposition is the removal of aerosol particles from the atmosphere by precipitation. Collection of freshly fallen snow, after a snowfall event, should therefore contain aerosols that were removed by the wet deposition process. Freshly fallen snow was obtained at Halley, with sampling triggered whenever the snow level, at an accumulation stake, rose by 1.5cm. (The experimental details of this are described in section 2.9.b(ii)). In total, up to 12 samples could be collected at one time, depending on how much accumulation the site received, with each sample holding 2.5 cm depth of snow.

An integrated accumulated snow concentration record is compiled using only samples

within the depth of fresh accumulation, as recorded at the snow stake. If accumulations were > 0.5 cm, but no accumulated snow samples were collected, a daily surface snow sample was added to the record. In some cases, a positive accumulation was immediately followed by a large negative one. In these cases, the appropriate samples from the top of the accumulated snow were removed from the data set. A record of snow that should have actually accumulated at the site is thus obtained.

These accumulated (fresh) snow samples will contain aerosol concentrations which we will assume are due to all the deposition processes. A total deposition flux can therefore be expressed as:

Equation (5.6)

$$F_t = C_{accum} S \rho_{snow}$$

where:

F_t = total deposition flux (ng cm^{-2})

C_{accum} = chemical concentration in accumulated (or fresh) snow (ng g^{-1})

S = depth of snow sampled (2.5 cm per sample)

ρ_{snow} = density of snow (0.4 g cm^{-3})

The wet deposition flux, is obtained by subtracting the fluxes (calculated throughout this chapter) for dry deposition, wind pumping, sublimation, blowing snow and fog, from F_t (Table 5.6).

Table 5.6: Estimates of the annual wet deposition flux at Halley during 1991 and 1992.

	Annual Wet Deposition Flux (ng cm ⁻² yr ⁻¹)
Species	Experimental Estimate
sea salt	59700
MSA	1750
nss sulphate	6900

5.9 Drifting and Blowing Snow Processes

Drifting and blowing snow has been found to alter the concentration of chemical species in Antarctic surface snow. Delmas & Jones, [1987] measured a 20% drop in sulphate concentrations, after a day of blowing snow, with no precipitation. Pomeroy et al., [1991] found concentrations in blown snow in Scotland to be 3 times higher than the original parent snow, and he found significant chemical alterations in drifted snow in the Canadian Arctic [Pomeroy & Goodwin, 1995].

At Halley, drifting snow is reported in the 3 hourly meterological record on 724 occasions, which corresponds to 131 days. Blowing snow occurs 359 times, on 44 days. Annually, 18% of observations at Halley, report blowing and drifting snow. At nearby Neumayer station, occurrences are reported in more than 40% of all meterological observations [König-Langlo et al., in press]. This frequency of events requires us to understand the processes of drifting and blowing snow and its role in deposition.

Blowing or drifting snow, affects the concentration of chemicals in surface snow in three

main ways. These are:

- 1 Redistribution of snow
- 2 Sublimation of drifting or blowing snow.
- 3 Scavenging of aerosol particles in the lower troposphere

After initial deposition, snow may be eroded and re-transported. This **redistributed snow** may be blown 10's of kms away from the original location [Tabler et al., 1990]. Once in the atmosphere blown or drifted snow, can mix freely with older or fresher snow. A snowfall event can be lifted from an area and deposited many km's away, resulting in complete deletion of the event from a particular area. In addition, a snowfall event from another area can be deposited at a different site, thus altering the surface snow concentration again. In general, it is assumed that deposition and removal of chemical species by blown or drifted snow should cancel one another out, and on average should have no effect on snow accumulation. However, this may not be the case for coastal Antarctic locations. As already described in chapters 3 and 4, sea salt concentrations in surface snow at Halley, are found to drop off with distance inland. It is therefore logical that winds from the west (from the coast), will bring in drifted and blown snow which has a higher sea salt concentration than winds from the east, (from the interior). Although this is difficult to quantify, it may be a significant factor in coastal Antarctica, but less so inland.

The second effect of drifting or blowing snow, on surface snow concentrations, is that of **sublimation**. Blown and drifted snow has a high surface area to mass ratio, and is therefore subject to intense atmospheric turbulence [Pomeroy & Jones, 1996]. As a result the potential for sublimation is high. In extreme blowing snow conditions, snow may be lifted

by turbulence 10's or 100's of metres into the atmosphere, where sublimation can then occur, reducing its mass to insignificance [Pomeroy and Jones, 1996]. At Halley, the sublimation rate from blowing snow during autumn and winter has been calculated using meteorological observations and theoretical models. King et al., [1996] determined the rate to be 3.71 mm water equivalent, for this 6 month period. More recent work by Mann, [personal communication] found this value to be between 2 and 6 mm water equivalent. During the summer, an upper limit of 15mm water equivalent has been determined [Mann, personal communication]. The accuracy of this value is limited by errors in the way the model calculates relative humidity.

The average annual accumulation at Halley is 324 mm water equivalent, calculated from snow stake measurements between 1973 and 1989 [King et al., 1996]. Using this value, sublimation during winter removes between 0.6 and 1.9% of the net accumulation. This small percentage is unlikely to have an important effect on chemical concentrations at Halley. During summer, this process removes 4.6% of the net total accumulation and may be more important at this time of year. At windier locations and sites of low accumulation, this process may again be more significant.

The final effect of blowing and drifting snow is the likely **scavenging of aerosol particles** from the lower troposphere. Aerosol concentration is almost certainly a function of height, with concentrations varying depending on what height the sample is collected from. This has already been put forward in chapter 3, as one reason for the lower mean annual aerosol

values found at Halley, in comparison with stations such as Neumayer. As the aerosol sampling at Halley takes place at no more than 2 metres above the surface, it is possible that sideward movement of drifting and blowing snow cleanses the air, before it is actually sampled on the filter faces.

The effect of the possible role of direct aerosol scavenging by drifting and blowing snow can be estimated by assuming that drifting snow completely cleanses a 5 m thick layer of air, and blowing snow a 50 m layer, on each day that it occurs. The sum of aerosol concentrations on the relevant days, when drifting or blowing snow occurred, is multiplied by the layer of air cleansed (Table 5.7). Assuming the air is not replenished by aerosol material from above, this will give an upper limit for the flux to the surface due to blowing and drifting snow scavenging.

Table 5.7: Estimates of the annual deposition flux at Halley due to scavenging by blown or drifted snow, during 1991 and 1992.

Species	Annual Deposition Flux due to Scavenging by Blown or Drifted Snow (ng cm ⁻² yr ⁻¹)
	Theoretical Estimate
sea salt	15
MSA	1
nss sulphate	4

Although the flux to the surface is estimated to be small (table 5.7), and therefore likely to have a negligible influence on the total annual flux, the effect of scavenging may be

enhanced if the snow particles previously passed over (and scavenged) a more concentrated air mass before reaching the sampling site. This could result in the scavenged air actually being more concentrated than the sampled air, particularly if the blown or drifted snow had passed directly over the sea on route. Also, if the near surface air is rapidly replenished with chemicals from above, the effect of scavenging would again be increased. However, as cyclonic activity is usually associated with blowing or drifting snow, frequent replenishment is unlikely, as during cyclonic activity the air mass tends to move vertically upwards. Also, as the flux values for this process are so small, a lot of replenishment could occur without affecting the significance of this process.

5.10 Fog Deposition Process

Fog is thought to be an efficient way of depositing chemicals onto the snow surface. Fog is a form of wet deposition, whereby cloud droplets reach the surface. The occurrence of fog indicates the presence of water at the Earth's surface, in the form of either liquid droplets, or ice crystals. Fogs are known to affect the concentration of surface snow, with increased chemical concentrations found in snow, after a fog event [Bergin et al., 1995; Kalina & Puxbaum, 1994; Davidson et al., 1989; Borys et al., 1988].

Fogs scavenge particles from the atmosphere, initially by condensation of supercooled water vapour onto aerosol particles, forming fog droplets. Droplets tend to be between 10 and 30 μm in diameter [Borys et al., 1992], and once formed have the ability to capture

other particles, in a process known as in-cloud scavenging [Davidson et al., 1996]. It is estimated that all aerosol particles with diameter $> 1\mu\text{m}$ or more, and more than half the particles with diameter $< 1\mu\text{m}$, can act as nuclei for fog droplets [Noone, 1992]. A significant number of particles which are scavenged by fog, are then deposited to the snow surface, at a rate known as the settling velocity. This is a similar term to the dry deposition velocity referred to throughout this chapter. The settling velocity is likely to be significantly greater than the dry deposition velocity for the original particles [Bergin et al., 1995]. Any fog droplets that do not reach the surface, evaporate, releasing their particles back into the air.

Fog deposition is also usually aided by the presence of rime [Davidson et al., 1996]. Riming occurs when supercooled water-drops coexisting with ice particles, collide and freeze on contact, causing the ice crystals to grow at the expense of the water-drops.

5.10.a Calculation of the Fog Deposition Flux

The contribution of fog to the deposition of chemical species to the snow surface can be expressed as:

Equation (5.7)

$$F_f = V_s C_f$$

where:

F_f = the fog deposition flux ($\text{ng m}^{-2} \text{s}^{-1}$),

V_s = the settling velocity of fog droplets (m s^{-1}) and

C_f = the chemical concentration in the fog droplets (ng m^{-3}) [Bergin et al., 1994].

The calculation assumes that only particles are scavenged, (not gases) and that nucleation is the only scavenging mechanism. It is also assumed that no additional uptake of particles occurs as the fog droplets settle [Davidson et al., 1996].

5.10.b Experimental Estimate of Fog Deposition

The extent to which fogs influence the chemistry of Antarctic snow needs to be estimated, by calculation of the fog settling velocity and fog deposition flux. At Halley, fog was recorded in the 3 hourly meteorological record 220 times, on 98 separate days in 1991 and 185 times, on 85 separate days, in 1992. This included 77 observations of “fog depositing rime” on 42 days during 1991 and 26 riming fogs on 12 days in 1992. To determine a deposition flux, only fogs that were depositing rime to the surface, will be included. This assumes that only riming fogs deposit, and also is somewhat subjective, depending on the meteorological observer. It is likely that riming fogs occurred at other times, but were not always recorded in the met record.

The fog flux can be determined experimentally by comparing surface snow concentrations for the day after rime deposits have occurred, with the day previously. For the 54 days when fog depositing rime was recorded, the snow stake measurements indicate that in all but one instance, accumulations were at or below 1cm. This is also the depth of sample collected by the surface snow sampling tool (see section 2.9.b(i)). Therefore, any riming

material deposited should be recorded in the surface snow collected.

Assuming that the sampler collects the top 1cm of snow only, and that the density of rime is 300 kg m⁻³ (the density of rime is considered to be lower than fresh snow), then 3 kg m⁻² of snow is collected [Wolff et al., in press]. Equation 5.7 can now be re-written as:

Equation (5.8)

$$F_f = \rho(C_n - (1-A) C_{n-1})$$

where:

F_f = the fog flux (ng m⁻²),

ρ = the mass collected per unit area (3 kg m⁻²),

C_n = the snow concentration after a rime event (ng kg⁻¹),

C_{n-1} = the snow concentration before a rime event (ng kg⁻¹) and

A = the ratio of the daily accumulation to the thickness of the sampled layer, which is taken as 1 cm

For the purpose of this calculation any negative accumulations were set to $A=0$. The values obtained give deposition fluxes for an individual day. A yearly fog deposition flux is calculated by summing F_f on the individual days when fog events occurred (Table 5.8).

5.10.b(i) Rimed Snow Experiment

In order to assess the affect of rime in the Antarctic, a short experiment was initiated and samples of rime were collected at various distances above the snow surface, on the Dyer Plateau, Antarctica (see section 2.11.c, for more information). Concentrations of rimed snow and surface snow are shown in figure 5.9.

Concentrations of chloride, MSA and nitrate in rimed samples were found to be close to that of surface snow. However, both nitrate and MSA (and also sulphate) appear to follow a trend, of increasing in concentration from the surface, and decreasing by a height of 1.10 m. The increase in concentration with height, for sulphate, is far more marked than the other species. Rimed samples seem to contain significantly more sulphate than surface snow.

The fact that we find rimed snow to be more concentrated than surface snow is not surprising. Part of the riming process, involves snow flake growth to incorporate significantly more amounts of super-cooled cloud water drops than traditional snow flake growth, such as diffusive growth. Diffusive growth results in the transfer of water from cloud water to snow, but does not include the distillation effect of evaporation, as rimed snow does. As a result, the rimed snow will tend to incorporate more chemical impurities than unrimed.

5.10.c Model Estimate of Fog Deposition

Estimates of the annual deposition flux due to fog, can be made theoretically, using a mathematical model. The model assumes a proportion of aerosol is taken up by fog drops, during a fog episode, and then removed to the surface by the settling of the droplets. This model can be expressed by the following equation [Davidson et al., 1996; Bergin et al., 1994]:

Equation (5.9)

$$F_f = h_f R C_{air} \left[1 - \exp \left(\frac{-V_s t}{h_f} \right) \right]$$

where:

F_f = the chemical flux to the surface due to fog ($\text{ng m}^{-2} \text{s}^{-1}$),

h_f = the fog height (m),

R = the dimensionless proportion of aerosols incorporated into fog droplets,

C_{air} = the concentration of aerosols in air, just before the fog event (ng m^{-3}),

V_s = the settling velocity of the fog droplets (m s^{-1}) and

t = the length of time the fog exists for (s).

For the purpose of this calculation, the fog height is taken as 150 m. This value is based on tethered sonde data for temperature, pressure and relative humidity measured at Summit, Greenland by Davidson et al., [1996]. A similar value for fog height is also determined using model data by Pandis & Seinfeld, [1989]. R , which is a measure of the concentration of air that is contained in fog drops, divided by the concentration of air just before fog formation, is taken as 1, and gives an upper limit for the fog flux. C_{air} is taken from the daily aerosol data at Halley. The settling velocity used is 0.007 m s^{-1} and was obtained by Borys et al., [1992] for fog droplets of $15 \mu\text{m}$ diameter. Finally, the fog duration is assumed to be 3 hours.

The results for this theoretical calculation are shown in table 5.8 alongside experimental determinations.

Table 5.8: Estimates of the annual deposition flux at Halley due fog depositing rime, during 1991 and 1992.

Species	Annual Fog Deposition Flux (ng cm ⁻² yr ⁻¹)	
	Experimental Estimate	Theoretical Estimate
sea salt	<2000	18
MSA	<30	1
nss sulphate	<200	6

The F_f values shown are all relatively small, in comparison with fluxes for other deposition processes. Even so, it is likely that the experimentally determined values are over estimated. This is due to the exclusion of negative deposition flux values, and thus ignores the large natural variability of snow concentrations. Also, other deposition processes almost certainly occur in conjunction with fog and rime events. Processes such as sublimation, and the effect of blowing and drifting snow are likely to also occur, and are indicated by some negative accumulations at the snow stake on these days. Based on these results, it seems that fog deposition at Halley is negligible. This is unsurprising as the percentage of days which have fogs at Halley, is small. Fogs occur 5% of the year, and fogs depositing rime, only 3%. Even assuming that all fogs deposit material in some way, the small percentage of occurrence makes its unlikely that they will play a significant role in annual deposition at Halley.

5.11 The Importance and Contribution of the Various Deposition Processes

The contribution that the various deposition processes described in this chapter make to the annual deposition flux at Halley is summarised in tables 5.9 and 5.10. The dominant process is that of wet deposition, the removal of aerosol particles from the atmosphere due to direct precipitation. This confirms findings in chapter 4, where individually high aerosol concentrations were only recorded in the snow record if coinciding with precipitation. Processes of fog deposition, wind pumping and blowing or drifting snow have a negligible effect on snow concentrations. Dry deposition, although much less significant than wet deposition, still accounts for around 10% of aerosol deposits and could be more, if large particles are important for sea salt.

Table 5.9: Summary of the annual deposition flux contributions to Halley

	Sea Salt ngm^{-3}	MSA ngm^{-3}	nss Sulphate ngm^{-3}
Dry deposition (expt)	<3060	<280	<870
Dry deposition (model)	1020	20	60
Wind pumping (model)	<200	<20	<60
Blowing/drifting snow	15	1	4
Fog deposition (expt)	<2000	<30	<200
Fog deposition (model)	18	1	6
Wet deposition (expt)	59700	1750	6900
TOTAL	66000	2100	8100

Table 5.10: Percentage contribution the various deposition processes make to the annual flux at Halley

	Sea Salt %	MSA %	nss Sulphate %
Dry deposition (expt)	<5	<13	<10
Dry deposition (model)	2	1	1
Wind pumping (model)	<1	<1	<1
Blowing/driftng snow	<1	<1	<1
Fog deposition (expt)	<1	<2	<3
Fog deposition (model)	<1	<1	<1
Wet deposition (expt)	90	80	85

In conclusion, wet deposition is found to be so dominant in this coastal Antarctic region, it must be this process that requires the focus of our future air-snow deposition studies.

Figure 5.1: *Integrated accumulation of snow at Halley, measured at a single stake, close to the sampling area for daily surface snow collection*

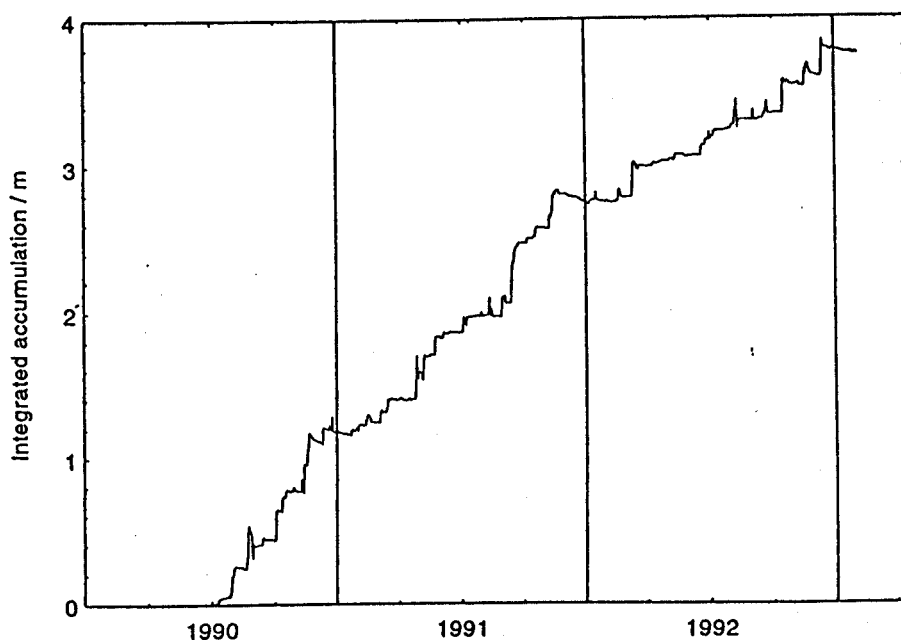


Figure 5.2: Concentrations of sea salt in surface snow at Halley when there was no significant accumulation measured at a snow stake. Days were selected if the accumulation was less than 0.5 cm and remained less than this for at least 4 days.

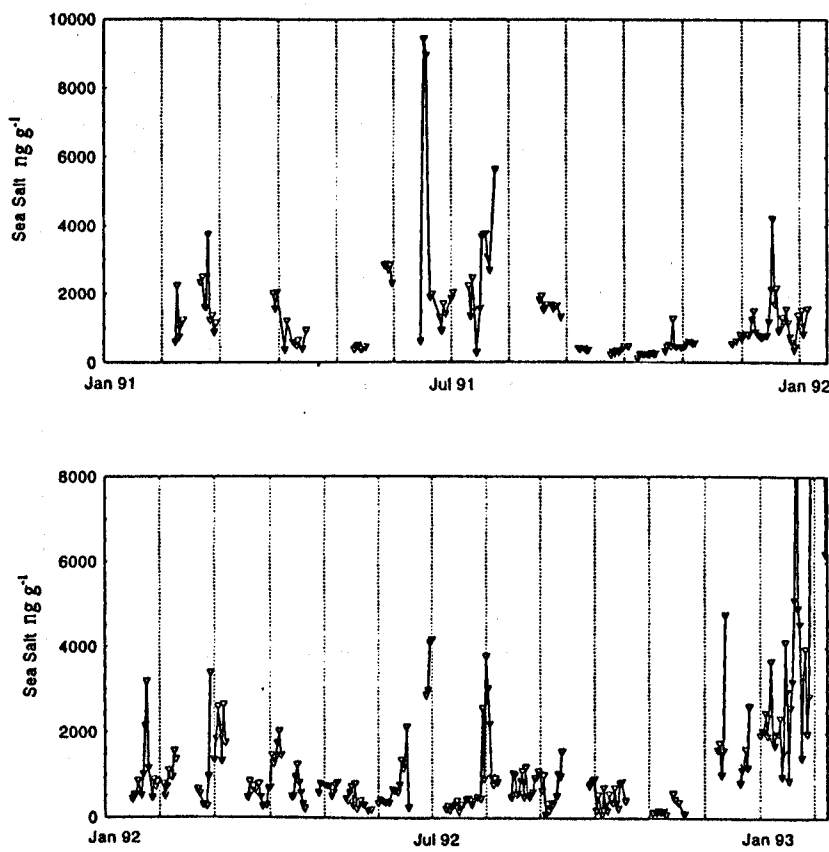


Figure 5.3: Concentrations of MSA in surface snow at Halley when there was no significant accumulation measured at a snow stake. Days were selected if the accumulation was less than 0.5 cm and remained less than this for at least 4 days.

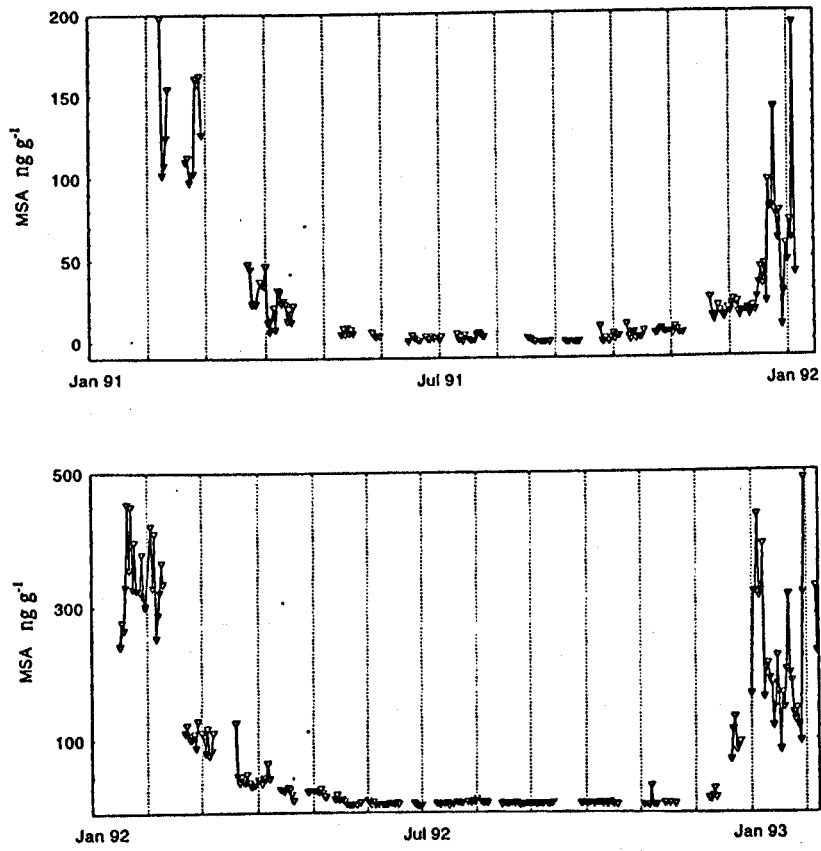


Figure 5.4: Sea salt concentrations for three events when no snowfall, drifting or blowing snow, or fog occurred and no accumulation was measured at the snow stake.

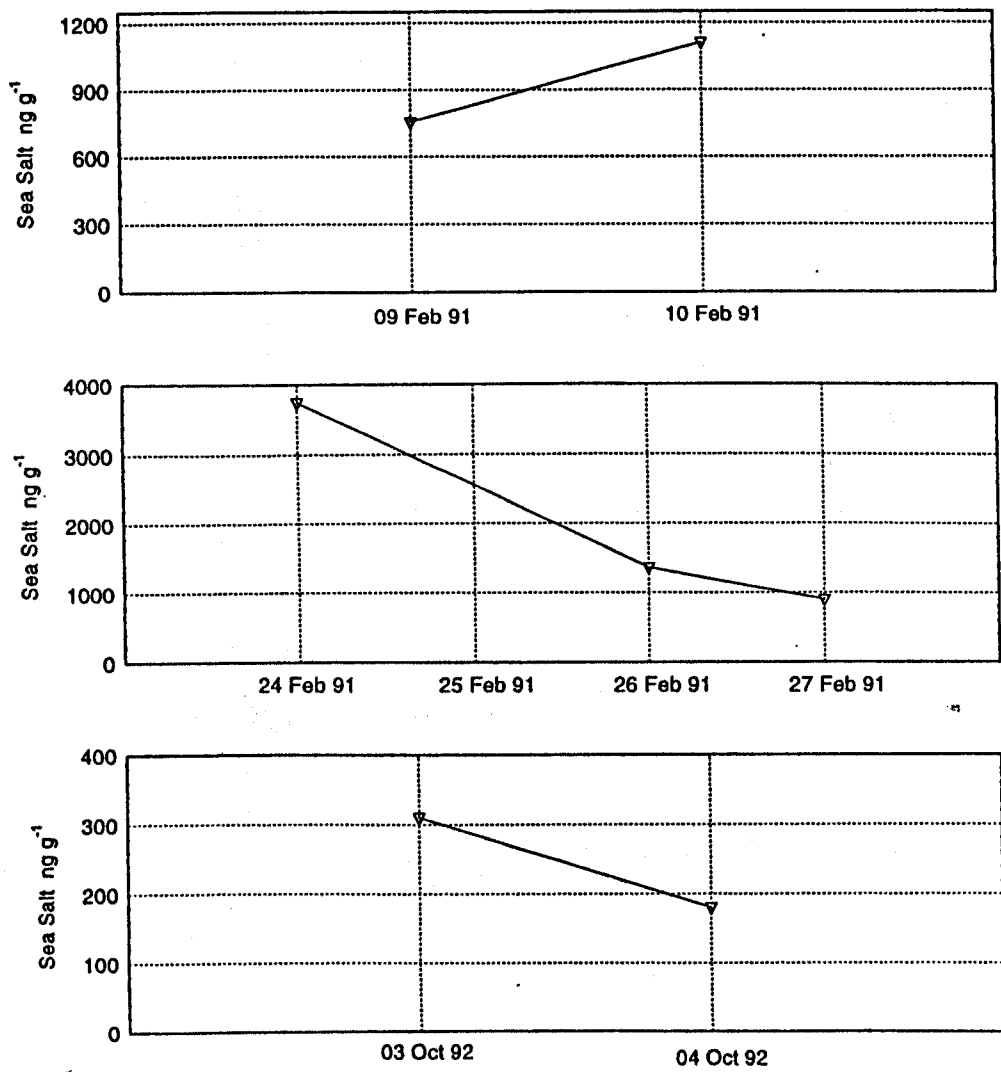


Figure 5.5: Scatter plot of daily changes in surface snow concentration against aerosol concentration at Halley for sea salt, on days when there was no significant accumulation and the daily concentration changes was limited to less than 100 ng g^{-1} . A best fit line is also superimposed on this plot and forced to pass through zero.

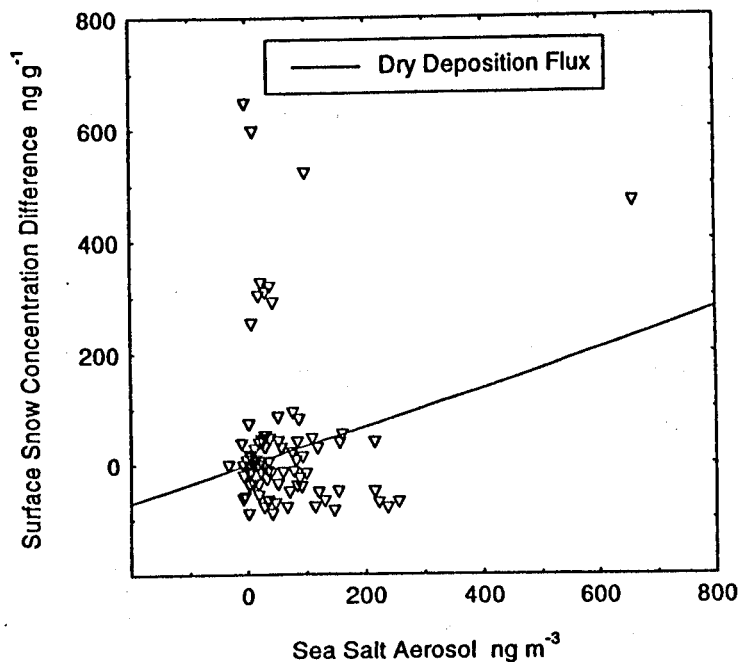


Figure 5.6: Deposition velocity versus particle diameter over snow at Dye 3, Greenland, based at a 10 cm height. Plots are shown for two different roughness heights (z_0), in a stable atmosphere [taken from Davidson, 1989].

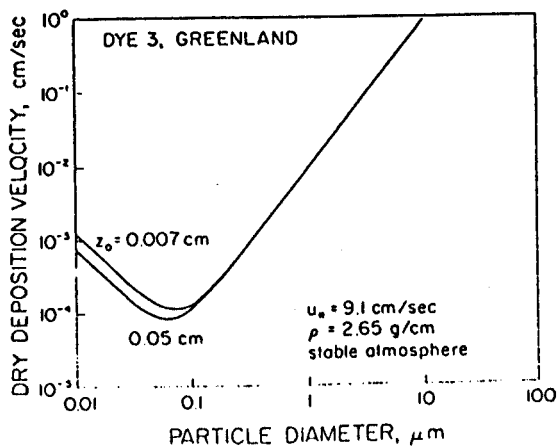


Figure 5.7: Schematic diagram of the sea salt concentrations in ng m^{-3} , found in six sastrugi features at Halley, during summer 1995. Four samples were collected from the face of each sastrugi, one sample from each side and two samples from the tail. Refer to figure 2.11 for details on exact sampling specifics.

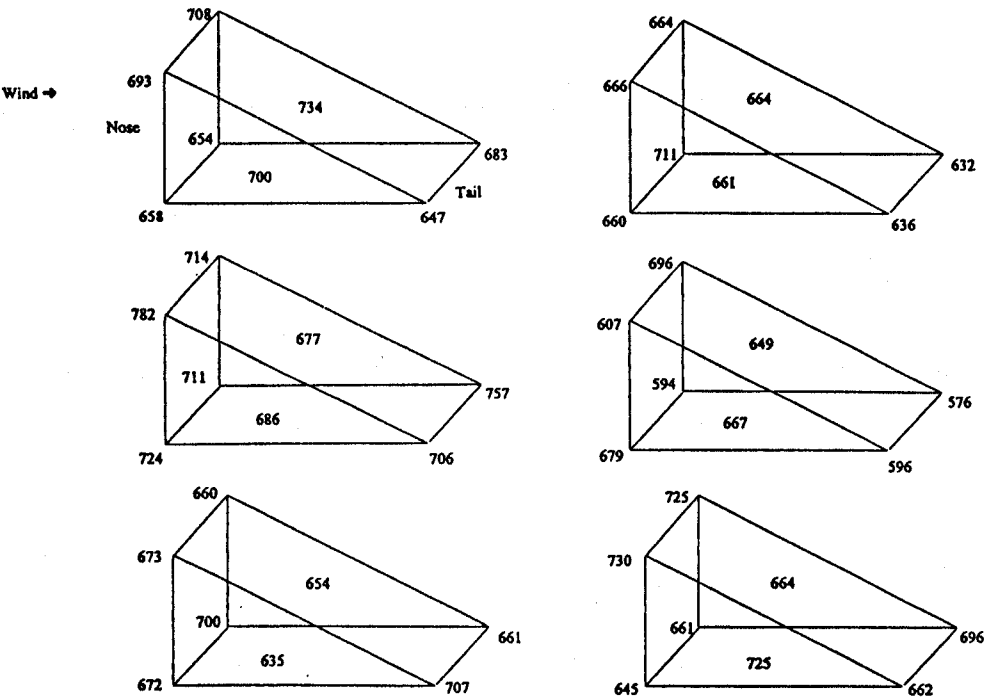


Figure 5.8: Scatter plot of accumulated snow concentration (fresh snowfall) against the preceding 24 hour aerosol concentration. A linear best fit line is superimposed onto the plots and represents the scavenging ratio for the species.

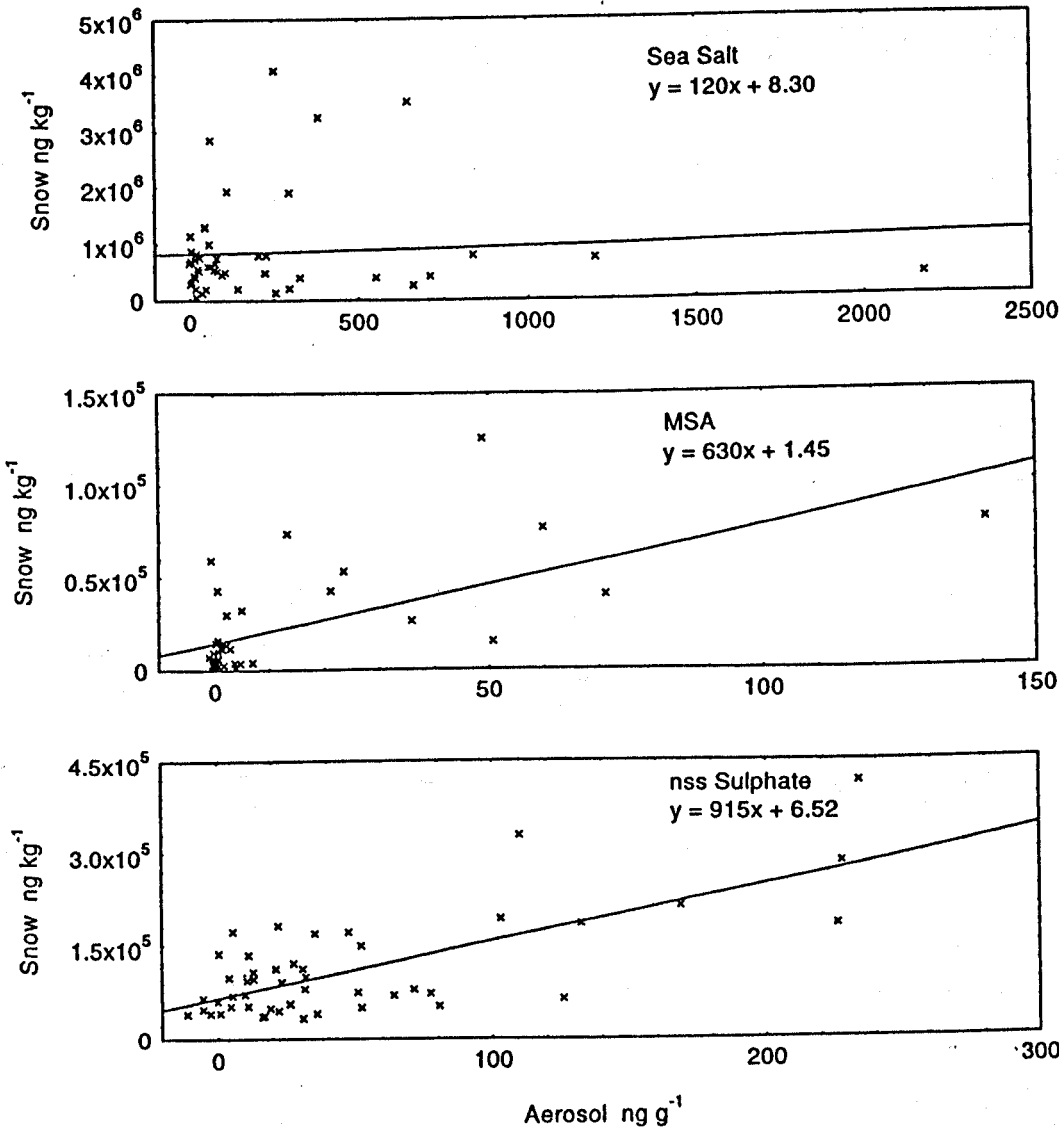
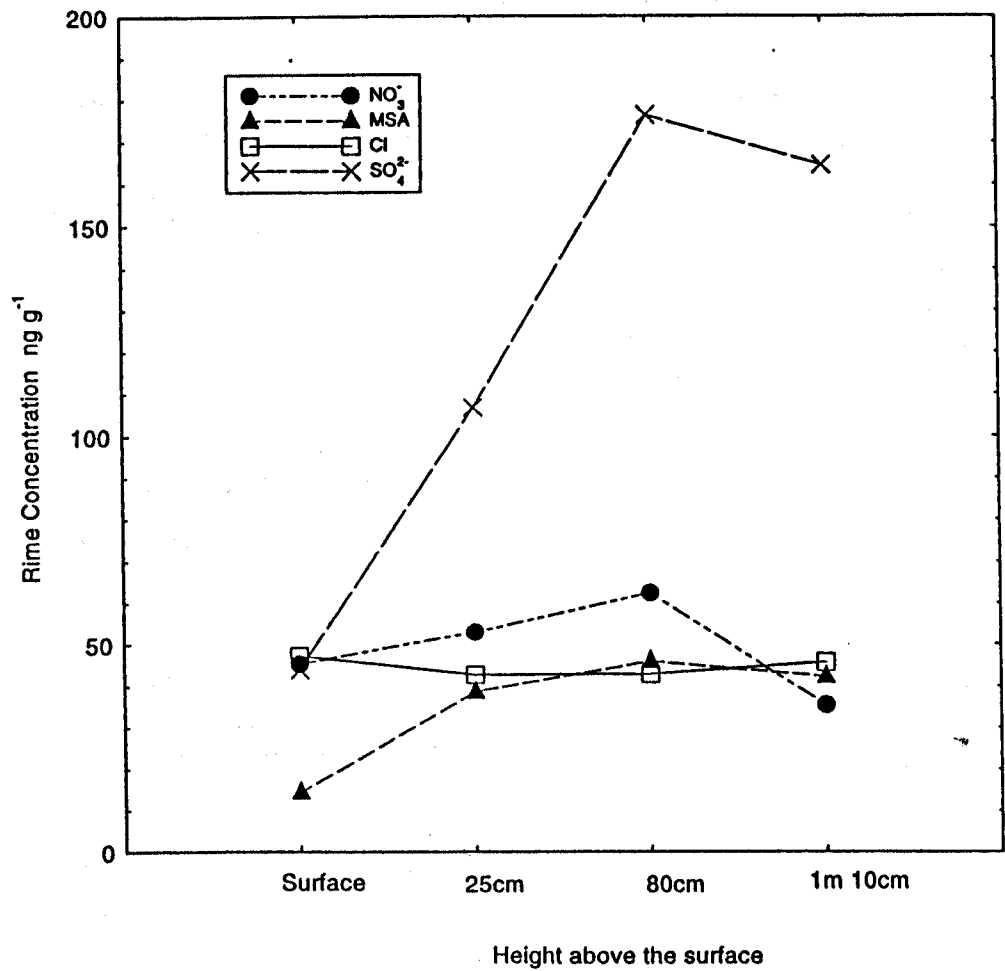


Figure 5.9: Concentrations of rime at three levels above the snow surface and also the concentration of surface snow at the site.



Chapter 6

Shallow Firn Cores in Coastal Antarctica

6.1 Introduction

In chapter 3, the sources of aerosol sea salt and non sea salt sulphate species at Halley were identified. Particularly high aerosol loadings were then traced into the surface snow record in chapter 4 and the means by which aerosols are deposited to the surface were discussed in chapter 5. This chapter, takes the process one stage further and asks to what extent is the snow record eventually preserved in coastal Antarctic ice?

To achieve the aim of this chapter, accumulated snow concentrations (see section 2.9.b(ii)) are compared with that of shallow firn cores. An integrated accumulated snow concentration record is compiled as described in section 5.8.c.

Three shallow firn cores are available (see chapter 2 for detailed discussion of firn sampling):

- Core 1: Sampled end January 1993 at Halley 5, covering both years of snow collection (analysed by E Pasteur)
- Core 2: Sampled end January 1992 at Halley 4, covering one year of snow collection at Halley 4
- Core 3: Sampled end January 1992 at Halley 5, covering one year of snow collection and used to compare the compatibility of the two Halley sites.

Also available are accumulated snow concentrations for July 1990 - January 1991. These samples were analysed by E Pasteur and have not previously been dealt with in this thesis. They are however, useful here, as the firn cores contain high loadings of sea salt and non sea salt sulphate for this period. Including data from these 6 months enables better interpretation and comparison of the firn cores and accumulated snow records.

Sea salt concentrations are discussed in terms of chloride in this section, as sodium data are not available for core 1. MSA concentrations are also examined and exhibit similar characteristics as non sea salt sulphate.

6.2 Sea Salt Species in Shallow Firn Cores

6.2.a Core 1

The accumulated snow and firn records have been plotted such that they can be relatively easily compared, using the same y-axis for both snow and core concentrations. Unfortunately, simultaneous snow pit density measurements were not made at the time of collection and snow and firn sample densities are therefore not known. The expected greater density of the firn (0.4 g cm^{-3}) compared to snow (0.3 g cm^{-3}) is evident in the

compression of peaks into a shorter depth in the firn core and this is as expected for the first 1-2 years.

Figure 6.1 shows the accumulated snow and firn core 1 records for chloride. Accumulated snow is shown with greatest accumulation equating to the most recent snow. The firn core is plotted with most recent snow at shallowest depths. The first thing to notice about figure 6.1 is that large chloride loadings at 2.3 m in the firn core are clearly seen in the accumulated snow. This corresponds to the 1990 sea salt maximum. Concentrations are approximately 30-40% lower in the core and this is probably due to the core being collected from Halley 5. The peak at 2.3 m (core) corresponds to snow sampled from Halley 4, some 15 km away from Halley 5 and closer to the coast. The difference in concentration reinforces the theory put forward in chapter 3, that sea salt has a very local source during winter at coastal Antarctic sites.

The winter 1991 maximum is also seen in the firn core (1.7 m), and has similar concentrations to that seen in the accumulated snow record. Elevated core concentrations at 0-0.2 m are not seen in the snow record. However, as the core was sampled several days after the snow sampling campaign stopped, it is possible that the snow containing the high chloride loadings was not sampled. In fact, a slight increase in snow concentrations is seen at the very start of the accumulation record (4.9 m), which may be the beginning of the peak seen in the firn core.

There are also some peaks in the accumulated snow record which are not seen in the core,

for instance, the small winter 1992 maximum at 4.2 m (snow). During this time, snow falls were not actually retained in the accumulated or the daily surface snow record and were in fact removed from the area by drifting or blowing snow.

6.2.b Cores 2 & 3

Firn cores 2 and 3 were sampled on the same day at Halley 4 (core 2) and Halley 5 (core 3), and cover the first year of snow sampling at Halley 4. Figure 6.2 shows that the two cores exhibit the same general features, with the Halley 5 core peaking slightly later, after 0.6 m. Only the end of the 1990 (1.4 m) chloride accumulated snow maximum is evident in the Halley 4 core (1.5 m) (Figure 6.2), and is completely missing from the Halley 5 core. Again, this indicates the very local nature of the aerosol sea salt source.

6.3 MSA in Shallow Firn Cores

6.3.a Core 1

Figure 6.3 shows that the MSA signal in the accumulated snow record is dominated by the strong seasonal peak in late summer, February/March. This seasonal signal is also seen in firn core 1, sampled after two years of snow collection at Halley 5. The summer maxima for 1992 and 1991 are clearly evident in both the core and accumulated snow records. The summer 1993 maximum however, which is just beginning to be recorded in the firn core (0.1 m), is not shown in the accumulated snow. This is due to snowfall removal by drifting

and blowing snow.

If we take a closer look at the firn record, the concentrations in the core for summer 1992 and 1991, are nearly 4 times less than those in the accumulated snow. A certain amount of concentration smoothing is to be expected, with concentrations likely to be less in a firn core than the snow record. Drifting and blowing snow will create this effect, with a redistribution of snowfall. It is also possible that MSA diffuses throughout a core [Mulvaney et al., 1992], however, this has never been reported in such short cores before. If the MSA accumulated snow record is smoothed (Figure 6.4), the summer 1992 peak has maximum concentrations that correspond more closely to those found in the firn core. However, the summer 1991 peak is still nearly 5 times larger in the snow, than firn.

Instead of diffusion effects, the large concentration differences between the firn and accumulated snow record for summer 1991 are probably the result of complete snowfall removal. It is possible that concentrations between 1.5-1.6 m in the snow record, have been physically removed from the snow surface, due to drifting and blowing snow. If we look again at chloride in core 1 (Figure 6.1), we can see that removal of the snow record between 1.5-1.6 m also removes a small chloride peak that is not seen in the core. The MSA peak seen in the core at 1.7 m in figure 6.4, is probably the tail end of the summer 1991 peak in the snow record (1.8-2.0 m). Differences in the concentration may also be because the snow record for 1991 was obtained from Halley 4 and firn core 1 was collected at Halley 5.

6.3.b Cores 2 & 3

Figure 6.5 shows core 2 (Halley 4) and core 3 (Halley 5) plotted with the accumulated snow record for one year. Both cores show the same general trends, with concentrations in the Halley 5 core peaking closer to the surface than Halley 4, after 1.0 m. Unlike core 1, accumulated snow concentrations for summer 1991 are comparable to cores 2 and 3. This implies that at firn core 1's sampling site, the early part of the 1991 summer peak was indeed removed, probably due to drifting snow. This did not happen at the location of cores 2 and 3 and implies that using a single years' data from sites can be flawed.

6.4 Conclusions

This study has shown that shallow firn cores do reflect accumulated snow concentrations. Factors such as densification and drifting or blowing snow, must be taken into account when interpreting a core. This is particularly so for drifting or blowing snow, as this process is likely to be a determining factor in whether a snowfall event is finally recorded in the accumulated snow record. The missing MSA concentrations in core 1 for summer 1991 has highlighted the caution which should be used in using just one years data from a site, as this could lead to unreliable information on the original atmospheric record. This is even the case for species (such as MSA) that are usually well defined by their strong seasonal cycle. Several years of firn and ice core data are needed to obtain an accurate picture of how a species is ultimately recorded in a core.

Figure 6.1: Two years of accumulated snow (lower plot) for chloride, sampled at Halley 4 and 5, and firn core 1 (upper plot), collected from Halley 5, after 2 years of snow sampling.

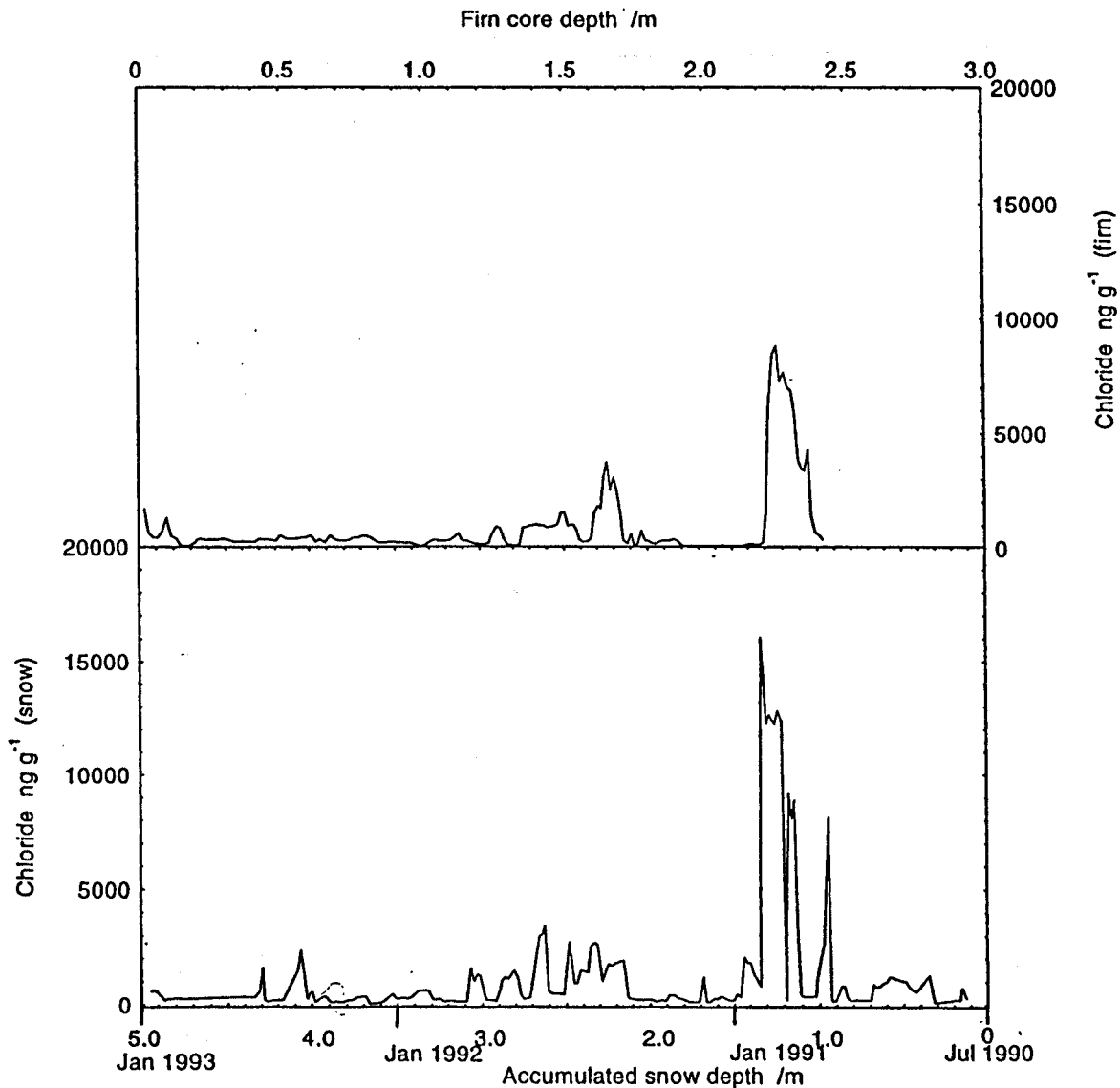


Figure 6.2: One year of accumulated snow (lower plot) for chloride and (upper plot) firn core 2 (Halley 4) and firn core 3 (Halley 5), sampled after 1 year of snow collection, at Halley 4.

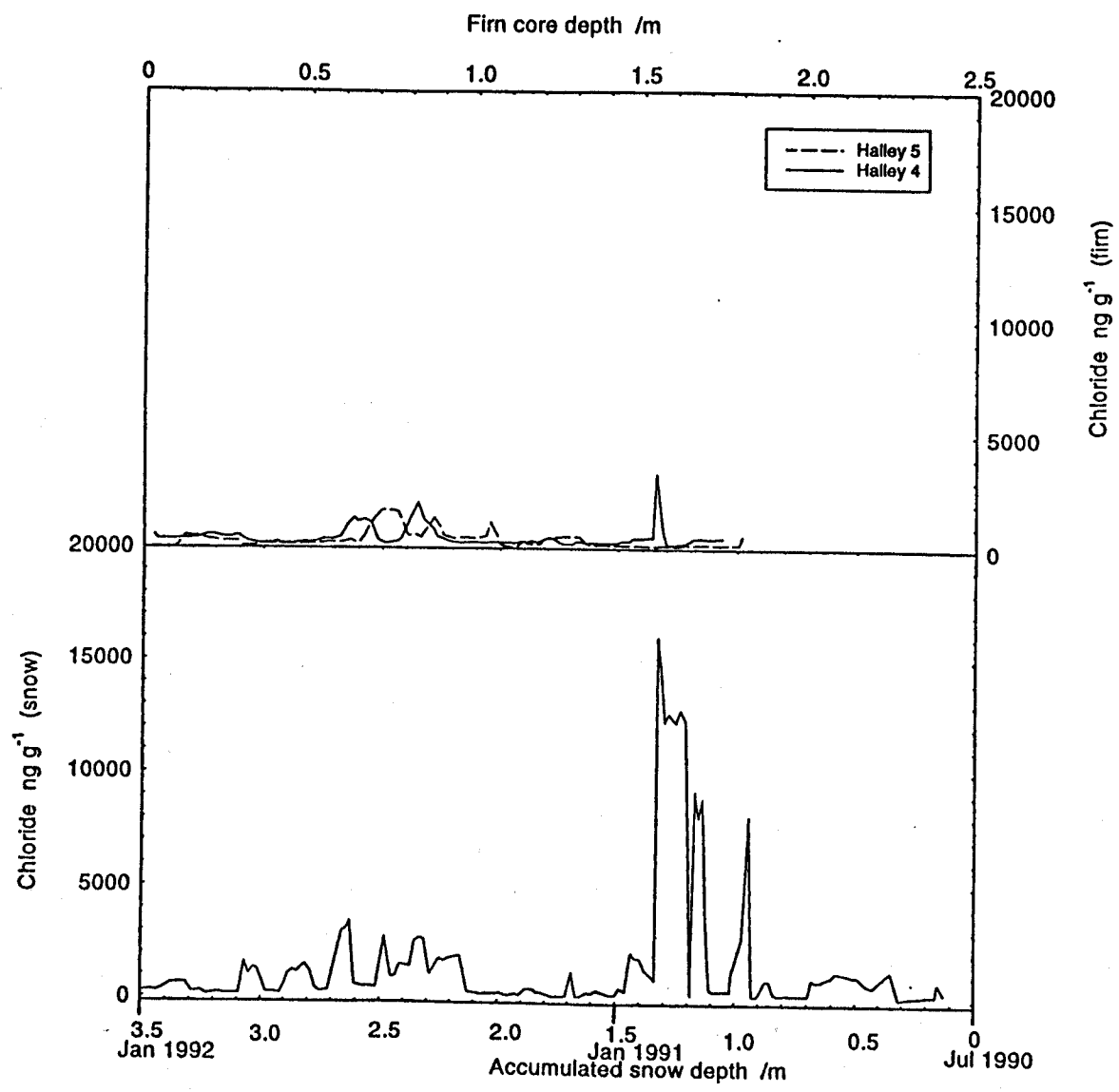


Figure 6.3: Two years of accumulated snow (lower plot) for MSA, sampled at Halley 4 and 5, and firn core 1 (upper plot), collected from Halley 5, after 2 years of snow sampling.

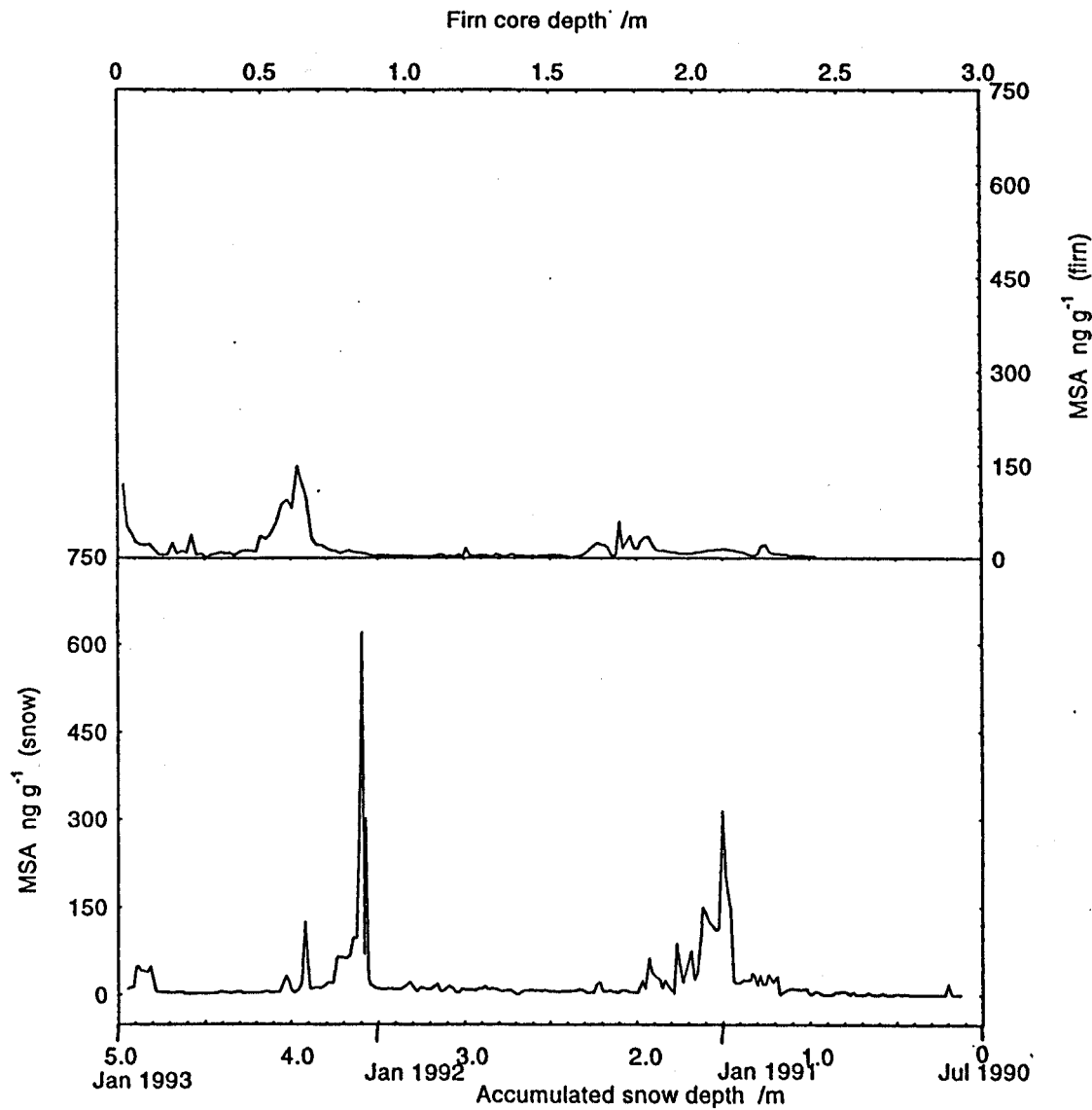


Figure 6.4: Smoothed signal of two years of accumulated snow (lower plot) for MSA, sampled at Halley 4 and 5, and firn core 1 (upper plot), collected from Halley 5, after 2 years of snow sampling.

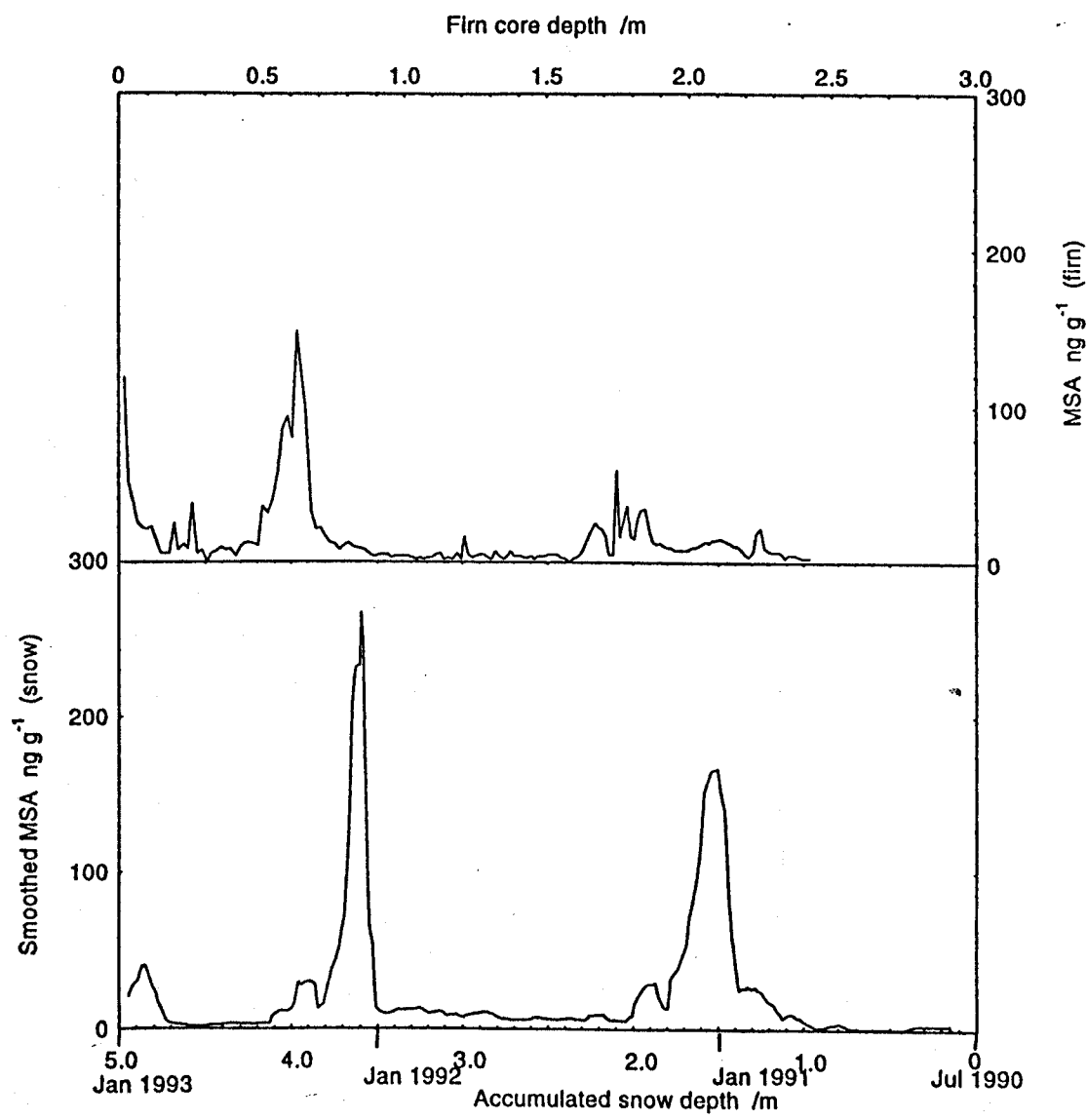
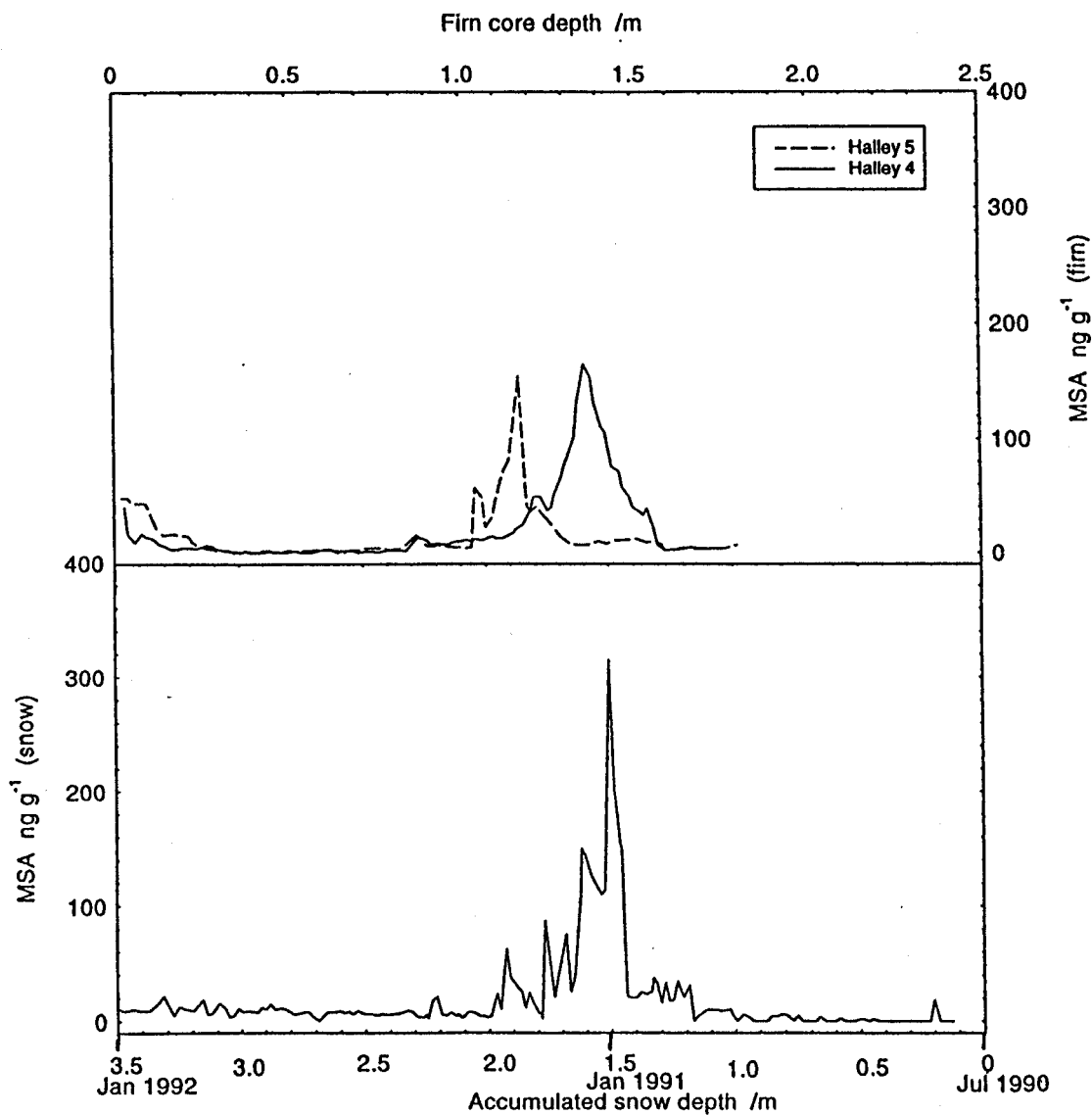


Figure 6.5: One year of accumulated snow (lower plot) for MSA and (upper plot) firn core 2 (Halley 4) and firn core 3 (Halley 5), sampled after 1 year of snow collection, at Halley 4.



Chapter 7

Conclusions

7.1 Introduction

The aim of this study has been to better understand the sources of aerosol particles reaching coastal Antarctica, and the processes that control aerosol deposition to the snow surface and inclusion into the ice. The ultimate aim is for this information to aid interpretation of ice cores. The thesis has concentrated on sea salt, methanesulphonic acid and non sea salt sulphate.

7.2 Summary

7.2.a The Source of Winter Sea Salt Aerosol at Halley

Aerosol sea salt at Halley is found to have maximum loadings during the Austral winter, with an annual mean of 162 ng m^{-3} . The seasonal cycle is characterised by a highly variable, spiky signal, with factor 60 concentration differences between several days.

The daily aerosol data available at Halley enables investigation of specific events, (such as

unusually high concentrations) with support from daily meteorological records. The aerosol sea salt concentration at Halley peaks during the winter months, when there is little open water in the area, suggesting that another source is important for winter sea salt aerosol. Rather than distant areas of open water, it has been suggested that this source is quite local, and consists of a thin layer of concentrated brine which sits on the surface of fresh, new ice. In addition to this, it is hypothesised that frost flowers (clusters of needle-like ice crystals, extending a few cm into the air), play a significant role in the incorporation of concentrated brine into the atmosphere. High wind speeds appear not to increase the likelihood of high episodes of sea salt and it is in fact the more moderate winds associated with a change in wind direction, which can be linked to this. A rapid fall-off in snow sea salt concentrations with distance inland, also indicates that the salt source is a local one.

Fractionation of the sea salt component, occurring during the winter, is found to occur in the Halley aerosol samples and has been previously reported in the literature. The probable sea salt source for this fractionation has been identified as the concentrated brine pools sitting on top of new sea ice surfaces [Wagenbach et al., in press]. The fact that high sea salt events, which dominate the total budget at this coastal site, were also found to be significantly fractionated, supports this theory.

There seems to be two potential sources of sea salt to Antarctica aerosol and snow: firstly, 'normal' sea salt, un-fractionated, from areas of open water and secondly, 'fractionated' sea salt, probably from newly formed sea ice surfaces. The relative areas of the two sources need to be determined. Source one will dominate in the interior and in air transported from

longer range. However, the concentration of sea salt will be more in the second.

Longer range air mass origin analysis was also undertaken, using a 5 day back trajectory model, for specific events of high winter aerosol sea salt. Air masses were categorised according to whether they passed over land, or ocean. Weekly, composite sea ice charts were also used to identify areas of open water in the ocean. The results showed that the origin of aerosol sea salt can not be identified by long range, back trajectory analysis. The air masses on days of high sea salt loadings were not in contact with open water, reinforcing the theory that sea salt has a very localised origin during winter, and that open water is not the source. It seems even more likely that local areas of freshly formed ice, housing pools of concentrated brine and frost flowers, are the dominant source for winter aerosol sea salt in the coastal region.

7.2.b The Source of MSA and Non Sea Salt Sulphate Aerosol at Halley

Aerosol methanesulphonic acid and non sea salt sulphate have maximum loadings during the Austral summer, and exhibit a broad winter minimum. The annual mean for MSA is 15 ng m^{-3} and 49 ng m^{-3} for nss sulphate. The strong seasonal cycle for both species has less daily variability than aerosol sea salt. However, concentrations between days can still vary by up to a factor 30, but are generally no more than a factor 9 different.

High events of aerosol non sea salt sulphate and methanesulphonic acid are compared with local meteorological events at Halley. No obvious link between high nss sulphate and wind

speed, direction or temperature, can be found. Instead, MSA and nss sulphate seasonal cycles follow that of oceanic, biogenic sulphur producers, for which DMS is the seasonal indicator. This confirms work by Minikin et al., [submitted] that uses satellite imagery of chlorophyll concentrations to indicate that marine biogenic activity, available to Halley during the summer (November to May), is likely to come from between 60°S and the continent's edge. During the winter (May to August), no marine biogenic activity takes place south of 60°S, determined by chlorophyll concentrations close to zero. Longer range transport dominates and DMS will tend to be available most from 50-60°S and north of 50°S, due to larger extent of sea ice. Further validating the thought that the source of MSA and nss sulphate is not a local one is the fact that snow concentrations decrease far more slowly, in comparison with sea salt, with distance from the coast.

Back trajectories for the majority of particularly high aerosol MSA loadings show that the air parcel of highest aerosol concentration had previously passed over the ocean. Sea ice charts also confirm that the individual back trajectory pathways, are over open water on these days. Trajectories for days when MSA is low in concentration, place the origin of the air mass generally either over the continent, or ice shelf, or over the ocean where the ice coverage is between 90-100%. It can be concluded that back trajectories can be used, with some success, to determine the origin of air and therefore predict high events of MSA. The high loadings of aerosol MSA do appear to have a longer range open water source that is not dependent on local meteorological events.

7.2.c Snow Record - Sea Salt and MSA

The snow sea salt record, does not follow a definite cycle. A strong maximum is seen during winter 1991, but this is not repeated in winter 1992. This may be attributed to spatial variability. The variability seen between days in the sea salt aerosol record is not as marked in the snow, which exhibits a more smoothed cycle. Short term variability does occur, but the peaks are not as sharp and tend to last for several days, rather than just one.

The strong seasonal cycle seen in the aerosol records for MSA and nss sulphate is repeated in the snow record, with both species strongly peaking during summer. The daily variability is similar to that seen in the corresponding aerosol record and once again is less marked than sea salt. High concentrations tend to last for several days, rather than sporadic, sudden increases.

7.2.c(i) High Aerosol Concentrations: are they seen in the snow record?

Episodes of increased aerosol sea salt and MSA loadings in air were compared with the corresponding snow records, to see how well elevated aerosol concentrations are preserved in the snow. For both sea salt and MSA individual inputs of high aerosol were not necessarily incorporated into the snow record. However, over a longer time scale, of a month or year, the main features of the aerosol record were generally found in the snow time series.

7.2.c(ii) High Snow Concentrations: are they seen in the aerosol record?

In general, high snow concentrations can be found in the aerosol record. However, the highest aerosol loadings are not necessarily recorded in the snow. Over a large time scale, the two records compare more favourably, but on an individual event basis, comparisons are harder to draw.

7.2.d Aerosol Deposition Processes

This work has established that high aerosol loadings are not always recorded in the surface snow. There must therefore, be special conditions and processes that enable aerosol deposition to occur. Using experimental data and theoretical models, the importance of each deposition process at Halley is quantified.

Although there are large uncertainties associated with these data, wet deposition is found to be by far the most dominant aerosol deposition process for coastal Antarctica. Dry deposition, although much less significant than wet deposition, could still account for around 10% of aerosol deposits. Processes of fog deposition, wind pumping and blowing or drifting snow appear to have a negligible effect on snow concentrations at Halley. Nevertheless, drifting snow plays a large role in determining which snowfalls are preserved in the snow record.

7.2.e Preservation of Coastal Antarctic Snow into Shallow Firn

This study has shown that shallow firn cores can accurately record accumulated snow concentrations. Factors such as densification and drifting or blowing snow, must be taken into account when interpreting a core. This is particularly so for drifting or blowing snow, as this process is likely to be a determining factor in whether a snowfall event is finally recorded in the accumulated snow record. However, caution should be used if only one years data is available from a site, as this could lead to unreliable information on the original atmospheric record. To be representative of an area, several years worth of data are necessary to obtain an accurate picture of how a species is recorded in the aerosol and snow records and most importantly, ultimately in an ice core.

7.3 Implications for Ice Core Interpretation

This thesis has suggested that for sea salt, non sea salt sulphate and MSA, there may be an alternate way of interpreting concentrations of these species in ice cores. For sea salt, the individual high concentration events dominate the total budget at Halley. These high, fractionated sea salt events, produced from concentrated brine on the surface of sea ice during winter, will be the values that eventually become incorporated into coastal ice.

Rather than the generally considered view that high sea salt loadings are associated with an increase in storminess and transport of aerosols from distant areas of open water, sea salt records from coastal cores may actually be giving us information on the extent of new, fresh

sea ice. If this is the case, the interpretation of sea salt ice core data may have been incorrect in the past. Sea salt concentrations in ice cores may therefore be used to infer the local temperature, sea ice extent and possible wind direction at the time of core formation.

For MSA and non sea salt sulphate, it is generally considered that high episodes of these species in ice cores, are the result of increased biogenic activity and increased DMS emissions at the time of formation. This work implies that in addition to this source, high aerosol loadings of MSA and nss sulphate could also give us information on the extent of open water. Any increases in ice core MSA concentrations could therefore be directly linked to a larger extent of open water.

This work has also identified that the process of wet deposition is so dominant that it can be considered to be the determining process at all coastal Antarctic sites, with just the efficiency of deposition altering, depending on weather conditions. Again, due to the significant present day dominance, in the past at coastal locations, it is likely to have been the controlling deposition process for sea salt, non sea salt sulphate and MSA. However, at inland sites, where accumulation rates are considerably lower, there may be more than one important deposition process. For central Antarctica, these deposition mechanisms must be identified.

7.4 Future Work

This project has shown that without a standard sampling protocol amongst research groups,

it can be very difficult to accurately compare aerosol and snow records from different sites. At the very least all aspects of the collection method should be reported. It would also seem prudent to continue with daily aerosol and snow resolution sampling at other sites around the coast and particularly in central Antarctica, where records are relatively sparse. Specifically, further sampling should be undertaken at Halley to confirm the pattern of the 2 years of aerosol and snow data obtained for this thesis. This will ensure that the results of this work are indeed typical for the location. Consideration should also be given to the need for aerosol and snow records from remote Antarctic locations, where ice cores are typically drilled. Aerosol and snow records from the nearest scientific base will not be adequate, particularly if the ice core drilling site is some hundreds of miles away from the nearest station. Instead, automatic aerosol and snow samplers are needed. At present, there are limited numbers of such equipment and this is a problem which must be tackled.

The sea salt fractionation process needs more investigation, so that in addition to current laboratory experiments, further evidence can prove where this process is occurring in the field. This will enable us to more confidently identify the source of winter sea salt aerosol. With this in mind, collection of the surface brine and frost flowers on fresh, new sea ice is needed to clarify the processes at work here.

The spatial extent of this proposed additional source for winter aerosol sea salt, (and the fractionation process), needs to be established to enable accurate interpretation of ice core records. It is almost certain that fractionation dominates the sea salt component at coastal locations, but the extent to which fractionation reaches into central Antarctica must be

further investigated. This is essential for the interpretation of ice cores and non sea salt sulphate concentrations from them, as any fractionation will affect the sea salt sulphate to sodium ratio used to calculate nss-sulphate values.

Further study is required to see if back trajectories and sea ice charts can be used to predict high aerosol loadings of MSA and nss sulphate. This would confirm the conclusion reached by this work, that open water is indeed a source of high aerosol non sea salt sulphate and MSA and not just increased marine biogenic activity.

Since it is so dominant, the process of wet deposition needs further study. This thesis has highlighted some problems associated with studying air-snow transfer processes at coastal Antarctic sites. For wet deposition, aerosol measurements at higher levels in the atmosphere (to avoid the possible effects of drifting snow) are certainly needed if this process is to be better understood. Aerosol concentrations made at ground level, may not be representative of concentrations at higher levels. The need for daily aerosol and snow sampling is again illustrated in the difficulties associated with determining scavenging ratios. The concentrations in long aerosol sampling periods are not representative of aerosol concentrations immediately before and during a snowfall. If daily snow samples are collected at a site, it is vital to know when these samples are actually fresh snowfalls. The Halley snow samples may have contained a memory of the aerosol concentration during a previous snowfall event, as samples were collected at a fixed time each day. The solution to these problems is not easy. It seems that determination of scavenging ratios may only be possible if aerosol samples are collected on top of tall towers, which makes filter

change difficult. A very short pumping time would also be required, to ensure the aerosol data only relates to a particular snowfall event. Both these solutions are very labour intensive and it is unlikely that an automated system could perform all these functions.

The effect of dry deposition has also been difficult to quantify here, with a continually changing snow surface presenting experimental problems. The use of surrogate surfaces, such as Teflon sheets, may provide the solution, as they offer a stable surface. This should be further investigated, but borne in mind that dry deposition velocities may vary depending on the type of surface used.

Although wind pumping was considered to be unimportant at Halley, this may not be the case for sites where accumulation rates are lower and sastrugi more abundant. It therefore seems prudent to study sastrugi features in more detail, to see if they are indeed subject to wind pumping effects. The same crop of sastrugi should be sampled over a period of several days, from formation to break-up. If possible, year round studies would be required, particularly at future ice core drilling sites.

The effect of drifting and blowing snow is particularly important to study further, with attention paid to whether sampling height plays a part in altering aerosol concentrations. Drifting and blowing snow should be considered important, as it is this process that determines whether aerosol particles deposited in the snow, actually remain there for long enough to become incorporated into the ice record.

7.5 Has the Aim of this Thesis Been Met?

The aim of this thesis was to increase our understanding of aerosol sources, and deposition processes, to the snow. The ultimate aim was to enable more accurate interpretation of ice core data, in terms of past atmospheric concentrations. In general terms, these aims have been met. This work has identified a new source for aerosol sea salt and confirmed that non sea salt sulphate and MSA have a long range source. Back trajectory analysis of air mass origins has shown that for MSA, this source is likely to be open water. With this information, we can properly assess what environmental changes can lead to changing concentrations in ice cores. The processes that control aerosol deposition to the snow surface have been quantified, and the dominant process determined. With this knowledge, at the very least, general trends in ice core concentrations can be explained and using present-day gross ratios between air and snow concentrations, estimates of past atmospheric concentrations can be made.

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